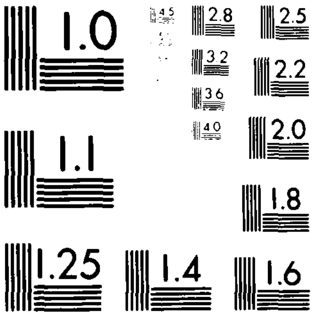
AD-A086 343 BATTELLE COLUMBUS LABS OH F/G 21/4
ANALYTICAL TECHNIQUES FOR AROMATIC COMPONENTS IN AIRCRAFT FUELS--ETC(U)
OCT 79 J S WARNER, R P KENAN F33615-78-C-2019
UNCLASSIFIED AFAPL-TR-79-2093 NL

1 OF 1
AD
A086343

END
DATE
FILMED
8-80
DTIC



MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

②

✓ AFAPL-TR-79-2093

ANALYTICAL TECHNIQUES FOR AROMATIC COMPONENTS IN AIRCRAFT FUELS

J. Scott Warner
Richard P. Kenan
Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

October 1979

TECHNICAL REPORT AFAPL-TR-79-2093

Interim Report for Period 15 June 1978 --- 30 June 1979

Air Force Aero Peopulsion Laboratory
Air Force Wright Aeronautic Laboratories
Air Force Systems Command
Wright Patterson Air Force Base, Ohio 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Paul C. Hayes Jr.

PAUL C. HAYES JR.
Project Engineer

Arthur V. Churchill

ARTHUR V. CHURCHILL
Chief, Fuels Branch

FOR THE COMMANDER

BLACKWELL C. DUNNAM
Chief, Fuels and Lubrication Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/POSF*, W-PAFB, OH 45433 to help us maintain a current mailing list".*

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AIR FORCE/56780/19 June 1980 — 60

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19 REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 18 AFAPL TR-79-2093

2. GOVT ACCESSION NO.: AD-A086343

3. RECIPIENT'S CATALOG NUMBER: 9

4. TITLE (and Subtitle): 6 Analytical Techniques for Aromatic Components in Aircraft Fuels .

5. TYPE OF REPORT & PERIOD COVERED:
Final Rep[redacted]t .
15 Jun[redacted]78 — 30 Jun[redacted]79

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): 10
Scott Richard
J. [redacted]/Warner [redacted]. P./Kenan

8. CONTRACT OR GRANT NUMBER(s): 15 F 33615-78-C-2019

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Battelle Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 16 30480594 17 05

11. CONTROLLING OFFICE NAME AND ADDRESS
Air Force Aero Propulsion Laboratory
Wright-Patterson Air Force Base, Ohio 45433

12. REPORT DATE: 11 Oct[redacted]79

13. NUMBER OF PAGES: 80

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): 12 87

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
aircraft fuels
aromatic hydrocarbons
gas chromatography
ultraviolet detector
photoionization detector
hydrocarbon type separation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An ultraviolet detector was shown to be highly satisfactory for the selective determination of aromatic components in jet fuels. The detector was operated at 208 nm and used with a glass capillary column gas chromatographic system. The detector gave a linear response in the range of interest and could detect individual benzenes and naphthalenes in jet fuels at levels down to 0.1% and 0.02% respectively.

A photoionization detector having a 9.5 ev source was found to be not sufficiently selective for aromatic hydrocarbons to be of value for fuel characterization. (Continued)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

407080

PREFACE

This technical report was prepared by the Analytical and Environmental Chemistry Section and Physical Sciences Section of the Columbus Laboratories of Battelle Memorial Institute. The work described was sponsored by the Air Force Aero Propulsion Laboratory (AFAPL), Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Contract No. F-33615-78-C-2019. The report covers the work performed during the period of 15 June 1978 to 30 June 1979.

Dr. J. Scott Warner, Battelle's Columbus Laboratories, was the Principal Investigator for the program and had the primary responsibility for the work described in this report. Dr. Richard C. Kenan, Battelle's Columbus Laboratories, was responsible for the optical design concepts presented. Mr. Paul C. Hayes, Jr., Air Force Aero Propulsion Laboratory (AFAPL), was the Project Officer.

A

TABLE OF CONTENTS

Page

SECTION

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS
(Continued)

LIST OF ILLUSTRATIONS
(Continued)

LIST OF TABLES

SUMMARY

An initial evaluation of the Perkin Elmer Model GC-55 ultraviolet detector was made to determine its suitability for determining aromatic components of aircraft fuels. The detector was used with both packed column and glass capillary column gas chromatographic systems. The best performance was obtained by using the detector at 208 nm with a glass capillary column system with no makeup gas. Approximately 35,000 theoretical plates were achieved with the system. Under these conditions benzenes and naphthalenes gave linear response curves over the range of 0.001% to 1.0%. Naphthalenes gave more than 10 times the response of benzenes. No response was obtained for petroleum ether or hexane used as a solvent indicating that the system was highly selective for aromatic components. In order to avoid overloading of the capillary column, aircraft fuels were diluted to 0.5% prior to analysis. The system could then detect individual alkylbenzenes in the fuel at levels down to 0.1% and alkylnaphthalenes at levels down to 0.02%. The system, therefore, looks extremely promising as a rapid and reliable method for characterizing the aromatic components of aircraft fuels.

Consideration was given to improving the performance of the UV detector by increasing the cell path length and minimizing dead volume and adsorption effects in the transfer line. Steps are being taken to evaluate other cell designs and a glass capillary transfer line.

An HNU Model PI-52 photoionization detector having a 9.5 ev source was evaluated as a selective detector for aromatic components in fuels. The relative response obtained for normal paraffins, cycloparaffins, toluene or xylene, and higher boiling aromatic hydrocarbons were approximately 1:3:6:25, respectively. This amount of selectivity was not considered sufficient to be of value for the characterization of fuels.

SECTION I

INTRODUCTION

Because of limitations on the supply of petroleum-based fuels, increasing amounts of alternate fuels derived from coal, shale oil, etc., will become available and will need to be considered as jet fuels. The Fuels Branch of the Air Force Aero-Propulsion Laboratory (AFAPL) is charged with developing jet fuel specifications that relate fuel chemistry to aircraft engine performance. Since the relative amounts of the individual aromatic components of a jet fuel are known to have profound effects upon the combustion properties the fuel, AFAPL is very concerned about the aromatic composition of possible alternate jet fuels.

At present there is no single reliable analytical procedure available for the routine detection, identification, and quantitative determination of individual aromatic components in a fuel. The objective of the current program is the development of such a procedure that is rapid and relatively inexpensive. The major emphasis is being placed on the modification and evaluation of an ultraviolet detector used with a glass capillary column gas chromatographic system. Prefractionation schemes, other detector systems, and spectrometric analysis methods are also being evaluated to determine their relative merits and to supply supportive data.

SECTION II

LITERATURE SEARCH

Computerized literature searches were made of Chemical Abstract sources for 1972 to 1978, Defense Documentation Center sources for 1952 to 1978, and National Technical Information Service sources for 1964 to 1978. The searches covered aromatic hydrocarbons in jet fuels as well as gas chromatography-ultraviolet detection. Over 400 references were cited. A review of the references showed that 19 were pertinent to this program. Those 19 references are given below along with a brief description of each one.

1. M. Inoue and D. Ishii, Kogyo Kagaku Zasshi, 74, 2045 (1971) (Japanese). C.A., 76, 41733d (1972).

   Continuous GC-UV and GC-IR was applied to xylene.

2. J. E. Longbottom, Anal. Chem., 44, 1111 (1972).

   A mercury-specific GC detector was designed that is based on UV absorbance and that has a sensitivity range of 0.05 to 100 ng.

3. A. F. Aksenov, et al., Khim. Tekhnol. Topl. Masel, 17, 41 (1972) (Russian). C.A., 77, 14206n (1972).

   The antiwear properties of hydrocarbons and additives in ramjet fuels were studied.

4. A. M. Kuliev, et al., Khim. Seraorg. Soedin., Soderzhashckekhsya, Neft. Nefteprod., 9, 479 (1972) (Russian). C.A., 80. 85462b (1974).

   Organic sulfur-containing compounds were studied for their effects on the thermal oxidation stability of jet fuels.

5. J. W. Robinson and J. P. Goodbread, Anal, Chim, Act, 66, 239 (1973).

   A vapor-phase fluorescence detector having a cell volume of 116 cm^3 was developed for the GC analysis of polynuclear aromatic compounds.

6. G. E. Ledyashova, et al., Tr. Groznen. neft. NII, 26, 53 (1973) (Russian). C.A., 83, 63162p (1975).

   Diethylene glycol was used to remove aromatics from aviation kerosene.

7. T. Tsuda and D. Ishii, Bunseki Kiki, 11, 511 (1973) (Japanese). C.A., 80, 78133s (1974).

   GC-UV and GC-IR are reviewed.

8. N. I. Vykhrestyuk, et al., Nefteperarab. Neftekhim. (Kiev), 9, 27 (1973) (Russian). C.A., 80, 135613z (1974).

Aromatic hydrocarbons in aviation kerosene were identified by GC-MS.

9. T. Tsuda and D. Ishii, J. Chromatog., 96, 171 (1974).

A GC-UV detector is described in which ethanol vapor is mixed with the GC effluent, then condensed and passed into a cell used for LC-UV.

10. D. Ishii, Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku, 25, 333 (1974) (Japanese). C.A., 84, 25352p (1976).

GC-UV was accomplished by mixing the GC effluent with ethanol vapor followed by condensation and use of a liquid cell.

11. G. F. Bolshakov and A. R. Belous, Zzv. Vyssh. Uchebn. Zaved. Neft Gaz, 18, 55 (1975) (Russian). C.A., 83, 149982t (1975).

Antiwear properties of different hydrocarbons and sulfur-containing compounds in jet fuels were studied.

12. R. A. Greinke and I. C. Lewis, Prepr., Div. Get. Chem., Am. Chem. Soc., 20, 787 (1975).

A GC-UV method involving trapping of GC peaks followed by UV analysis was used to monitor petroleum pitch volatiles.

13. J. N. Driscoll and F. F. Spaziani, Research/Development, 50, (May 1976).

A photoionization detector for GC work is described.

14. V. A. Smeyanov, V. A. and E. P. Seregin, Khim. Tekhnol. Tapl. Masel, 3, 7 (1976) (Russian). C.A., 85, 48943s (1976).

A review is given in which additives, antiwear properties, storage stability, oxidation induction period, and effects of aromatic hydrocarbons in jet fuels are discussed.

15. F. Korber, Report No. FTD-1D (RS) I-1174-76, Foreign Technology Division, WPAFB, November, 1976.

The ignition behavior of aviation fuels and some hydrocarbons of uniform composition is reported.

16. M. C. Pankova, et al., J. Chromatog., 137, 198 (1977).

Bicyclic aromatic hydrocarbons in kerosene were separated by preparative GC and characterized by UV spectroscopy.

17. J. N. Driscoll, J. Chromatog., 134, 49 (1977).

A photoionization detector for GC work and with a detection limit of 2 pg for benzene is described.

18. P. M. Houpt and G. H. W. Baalhuis, Appl. Spectrosc., 31, 473 (1977).

A second derivative UV spectrophotometer is described which used a 3 ml cell with a 1-meter path length and which can be used with a GC.

19. F. N. Hodgson, H. C. Tucker, and R. D. Butler, Report No. AFAPL-TR-77-60, Interim Technical Report from Monsanto Research Corp., November, 1977.

An ultraviolet detector which responds only to aromatic petroleum constituents was designed and tested for the GC analysis of jet fuels.

SECTION III

EXPERIMENTAL STUDIES

Liquid Chromatographic Fractionation Studies

One approach to determining the aromatic composition of jet fuels involves the fractionation of the fuels into nonaromatics and aromatics prior to analysis by gas chromatography. In studies on other programs we have obtained aromatic fractions of crude oils by gravity-flow column chromatography using a special grade of activated silica gel and elution of saturates with petroleum ether followed by elution of aromatics with a mixture of petroleum ether and benzene or methylene chloride. The aromatic fractions were concentrated by solvent evaporation.

Jet fuels, however, are relatively volatile and often contain benzene as one of the aromatic components. Consequently concentration by solvent evaporation and the presence of benzene in the elution solvent can not be tolerated. The fractionation procedure was therefore modified to avoid solvent evaporation and to use methylene chloride for the elution of aromatics. The concentrations of components in the eluted aromatic fraction were sufficient to permit gas chromatographic analysis using a flame ionization detector without solvent evaporation. The details of the fractionation procedure used are given in Appendix A. Six jet fuel samples supplied by the Sponsor were fractionated using this method and were analyzed by gas chromatography as described below.

Capillary GC and GC-MS Analysis of Fuel Samples

The aromatic fractions obtained from silica gel fractionation of six jet fuel samples supplied by the Sponsor were analyzed by GC and GC-MS using an SE-54 glass capillary column system that achieved approximately 75,000 theoretical plates. For the GC analysis a Hewlett Packard Model 5730 gas chromatograph with a flame ionization detector and subambient capabilities was used. The column oven temperature was programmed from 0 to 200°C at 2 degrees per minute. The amount of sample injected using a split ratio of 10:1 was 2 µl of an approximately 0.05% solution in methylene chloride.

The GC-MS analyses were performed under similar conditions using a Finnigan Model 3200 quadrupole mass spectrometer interfaced with a Finnigan Model 9500 gas chromatograph and a System Industries Model 150 data system. The individual aromatic components in the samples were tentatively identified on the basis of their mass spectra and retention times. The GC-MS total ion chromatogram from the aromatic fraction of, a sample of Paraho JP-4, which contained nearly all of the components present in all six jet fuel samples studied, is given in Figure 1. The mass spectral identifications or tentative identifications of 94 components found in Paraho JP-4 are given in Table 1.

Gas chromatograms of the aromatics from the six fuel samples studied are shown in Figures 2 to 7. The component identifications are those given in Table 1. This information was used as a guide to UV detector studies.

Ultraviolet Detector Evaluation

A Perkin Elmer Model GC-55 ultraviolet detector was purchased for this program and evaluated using packed column and capillary column systems. The detector was interfaced with a Varian Model 2840 gas chromatograph that was equipped for capillary column studies as well as packed column studies.

Packed Column Performance

The initial evaluation was performed using a packed column, a 3m x 2mm I.D. glass column packed with 3% OV-101 on Gas Chrom Q. The practical detection limit for an alkylbenzene in such a system was about 500 ng (1 μl of a 0.05% solution) at 254 nm. Six jet fuel samples supplied by the sponsor were analyzed by the system using 2 μl injections of a 2.5% solution in hexane. The column temperature was programmed from 100° to 200°C at 8 degrees per minute. The UV detector was operated at 254 nm in the absorbance mode with an attentuation of x16. Any decrease in the attenuation gave excessive noise. By operating in the absorbance mode the response increases linearly with concentration. Gas chromatograms of the six jet fuel samples obtained under these conditions are given in Figures 8 to 13. As indicated by the chromatograms, the detector readily

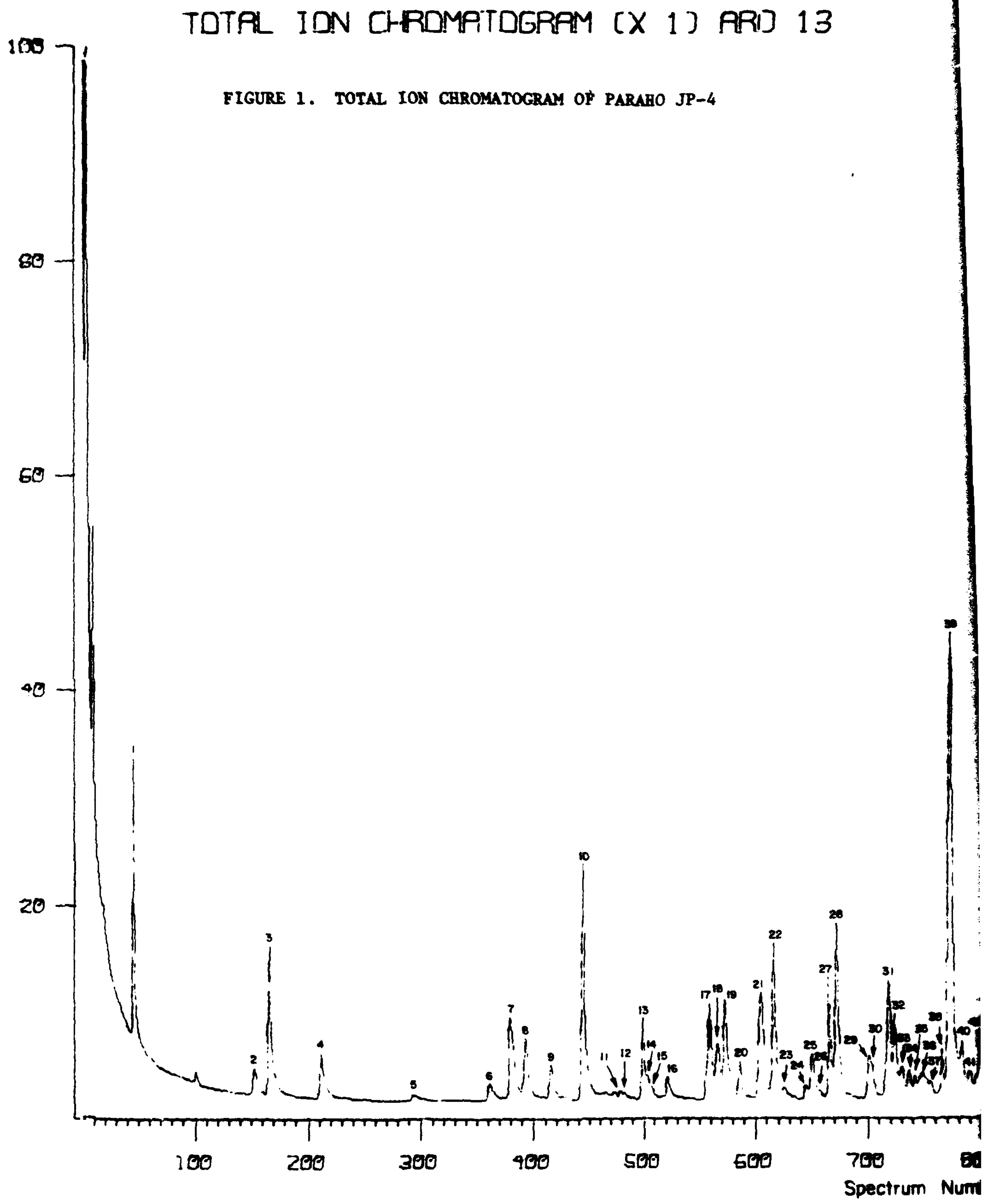
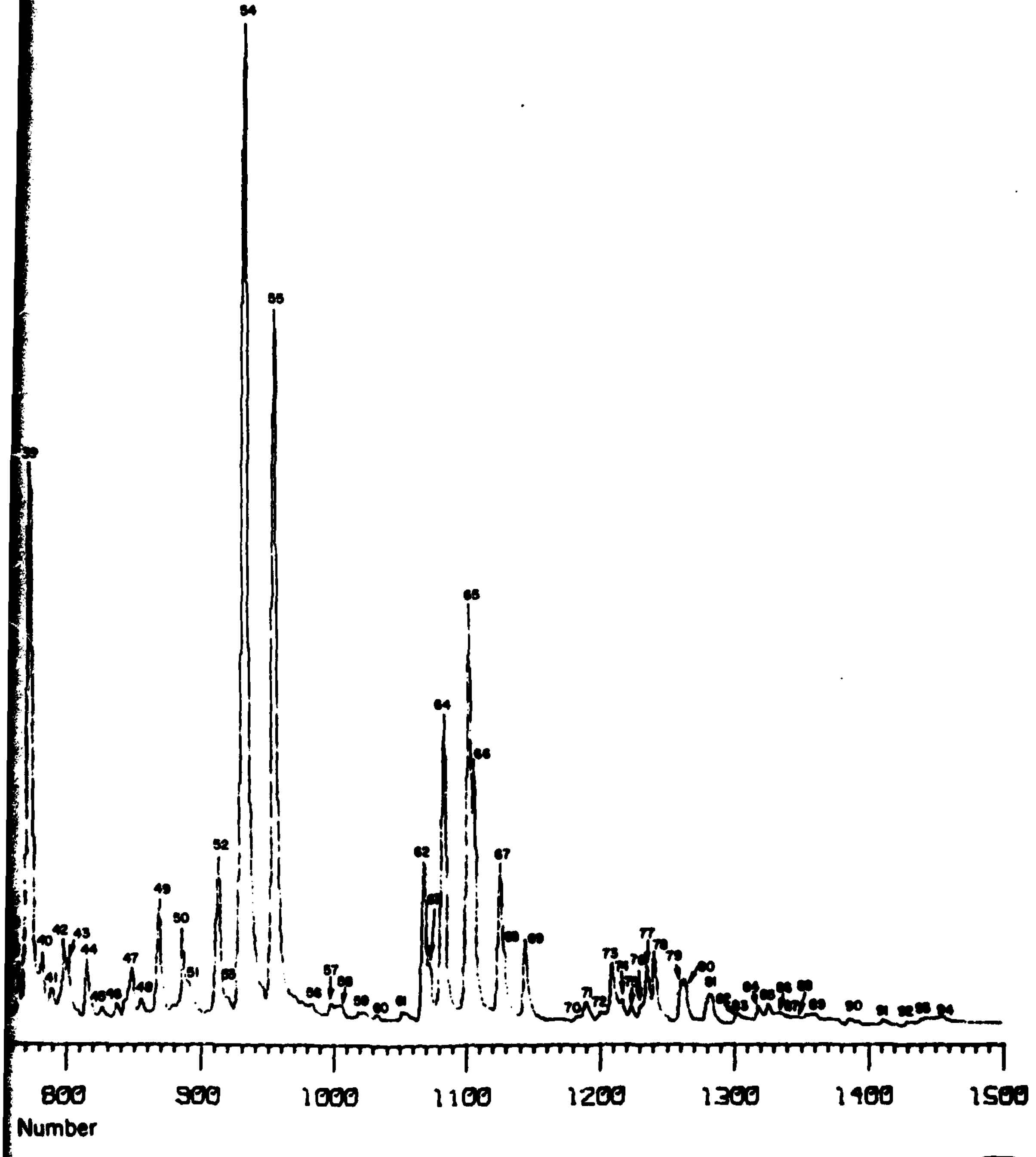


FIGURE 1. TOTAL ION CHROMATOGRAM OF PARAHO JP-4


39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
800
900
1000
1100
1200
1300
1400
1500
Number

2

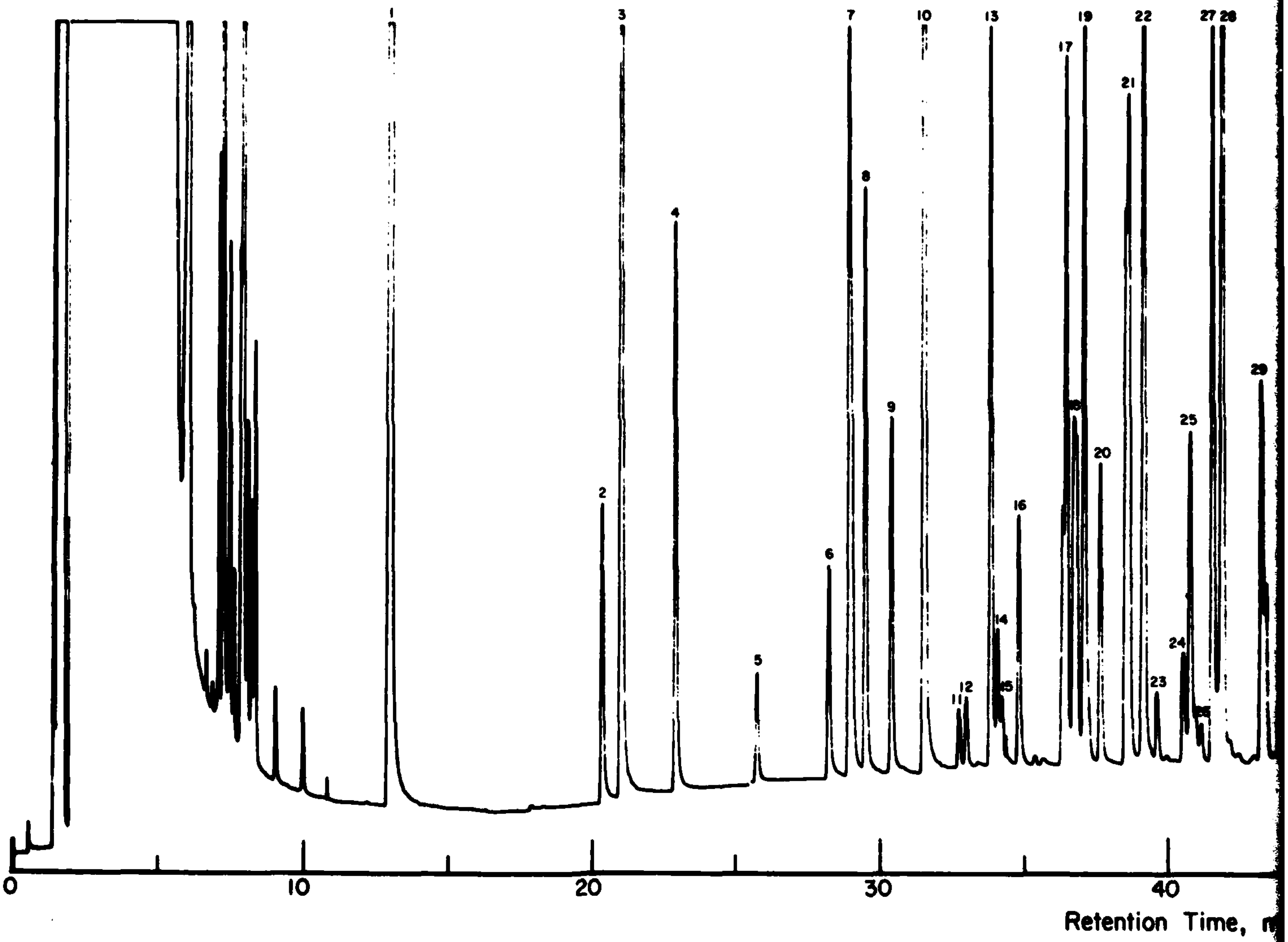
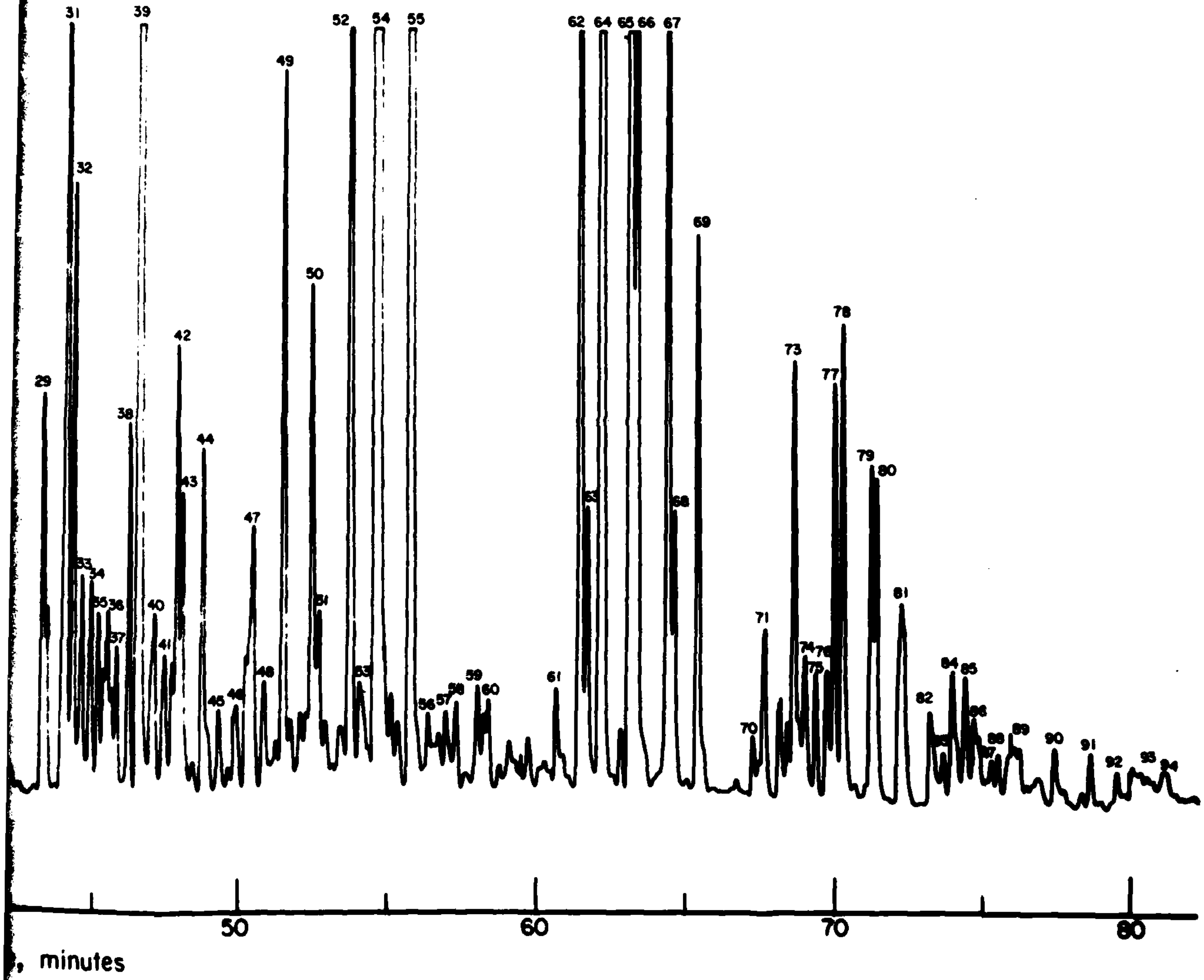


FIGURE 2. FID GAS CHROMATOG



OGRAM OF PARAHO JP-4

2

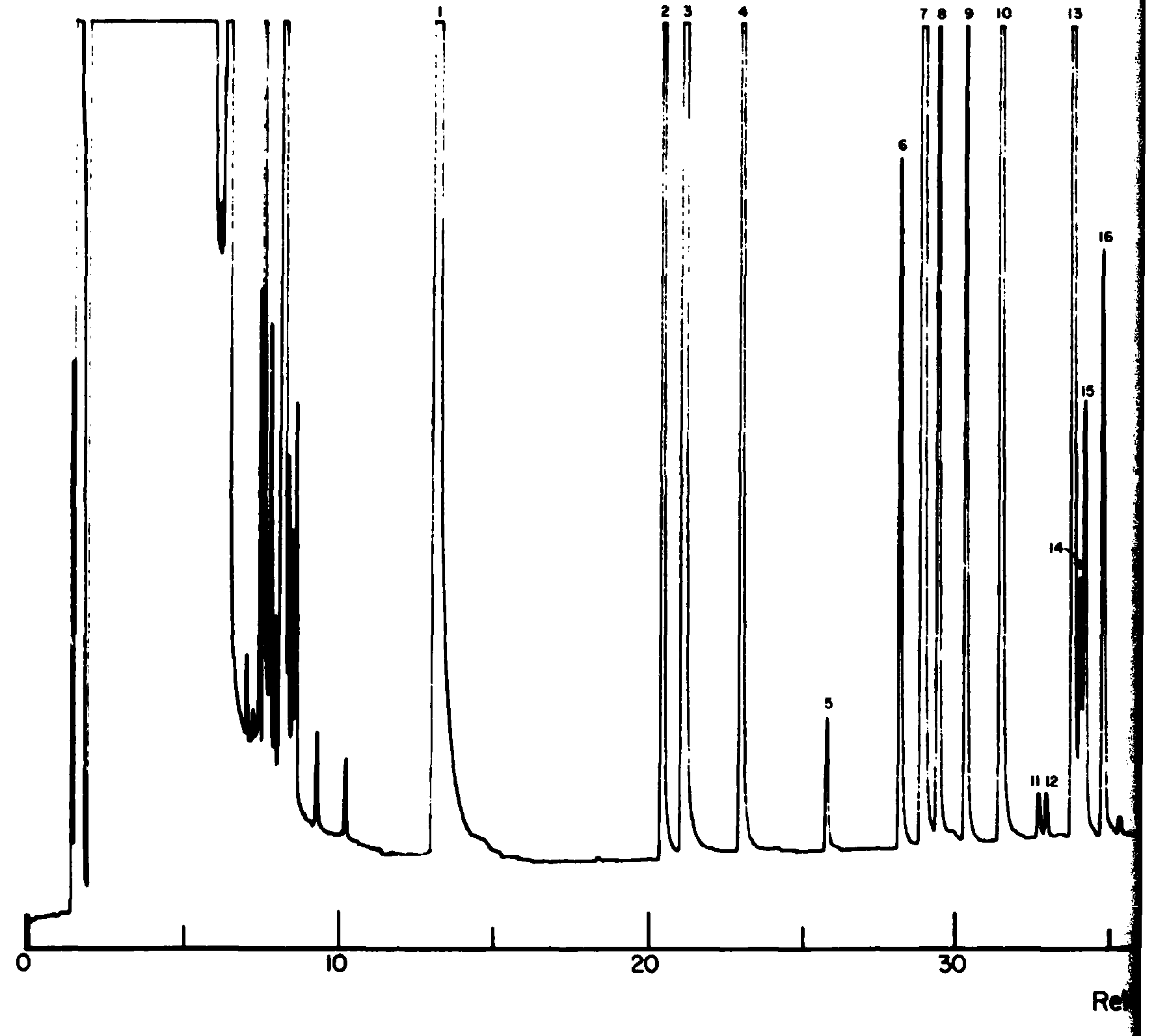
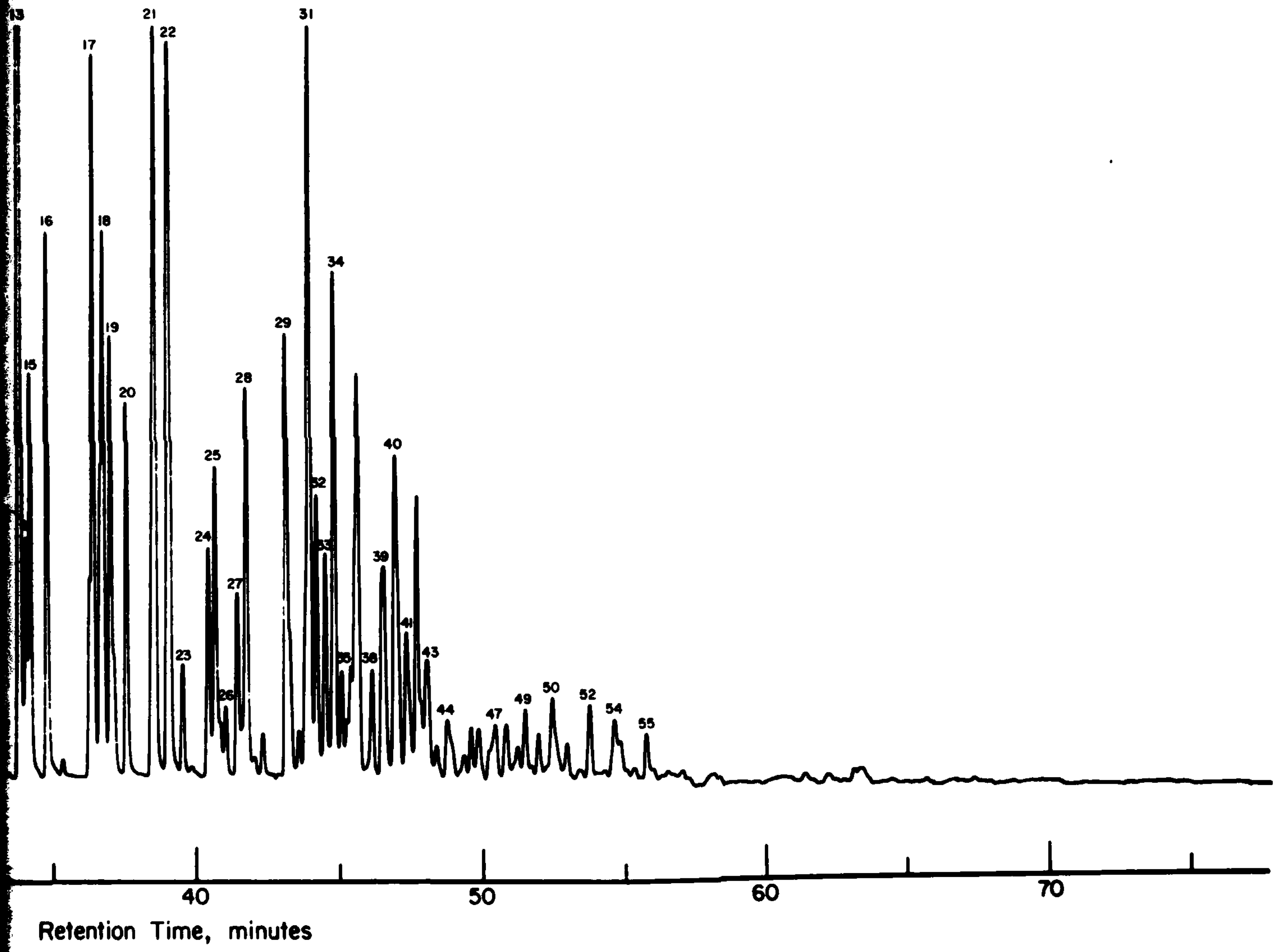


FIGURE 3. FID GA



D GAS CHROMATOGRAM OF SHALE OIL JP-4

2

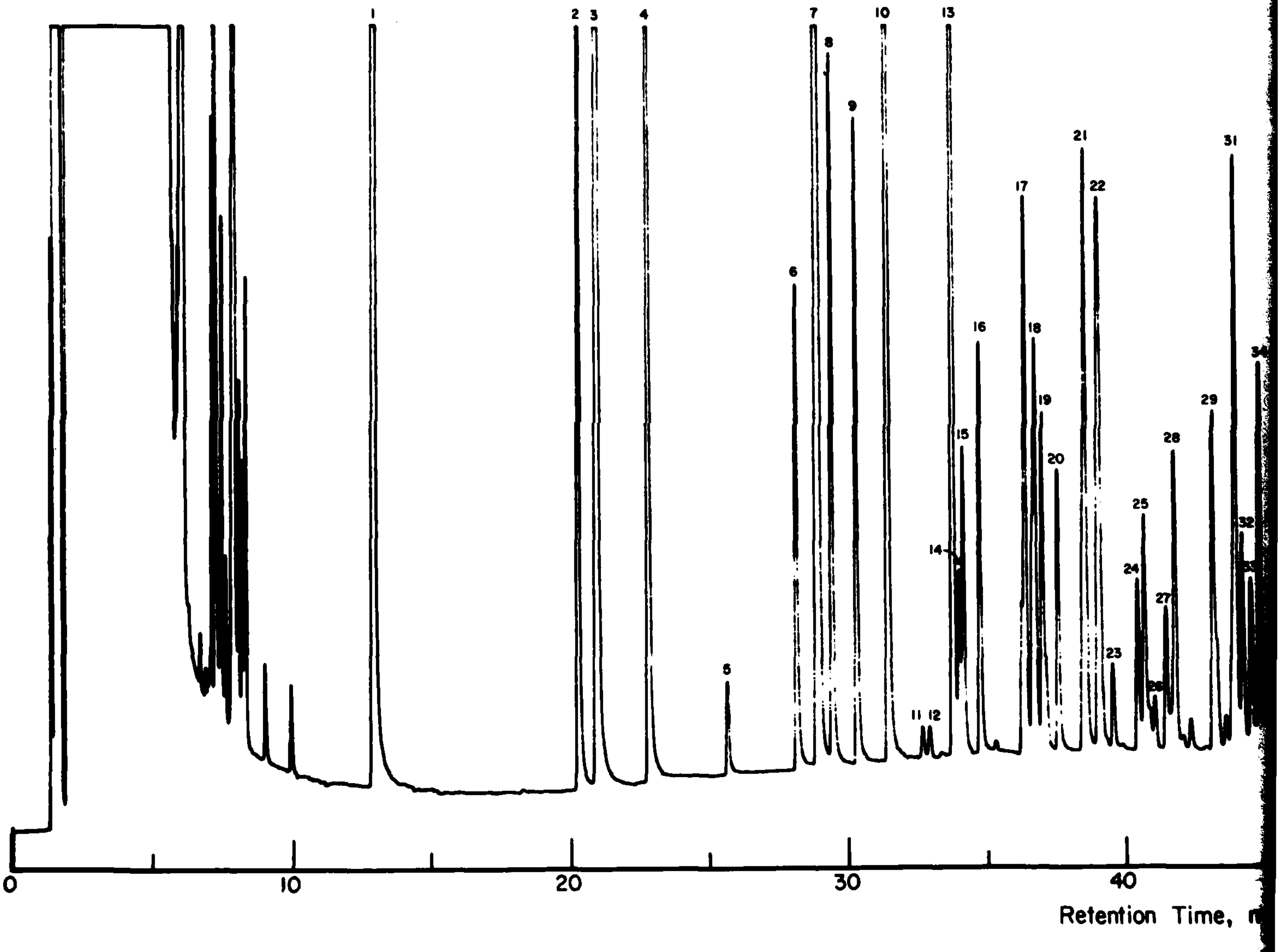
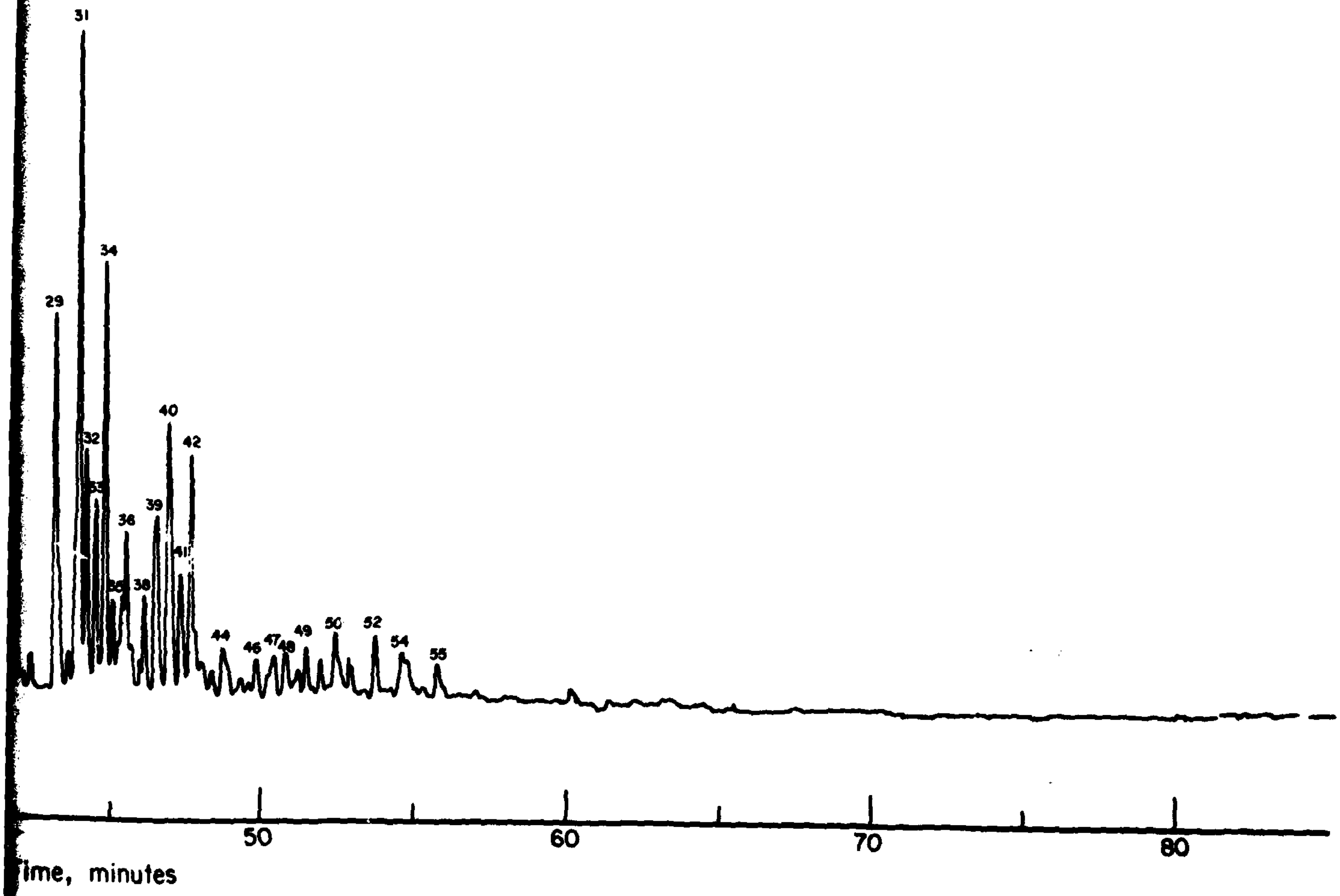


FIGURE 4. FID GAS CHROMATOGR



ATOGRAM OF SYNCRUDE JP-4

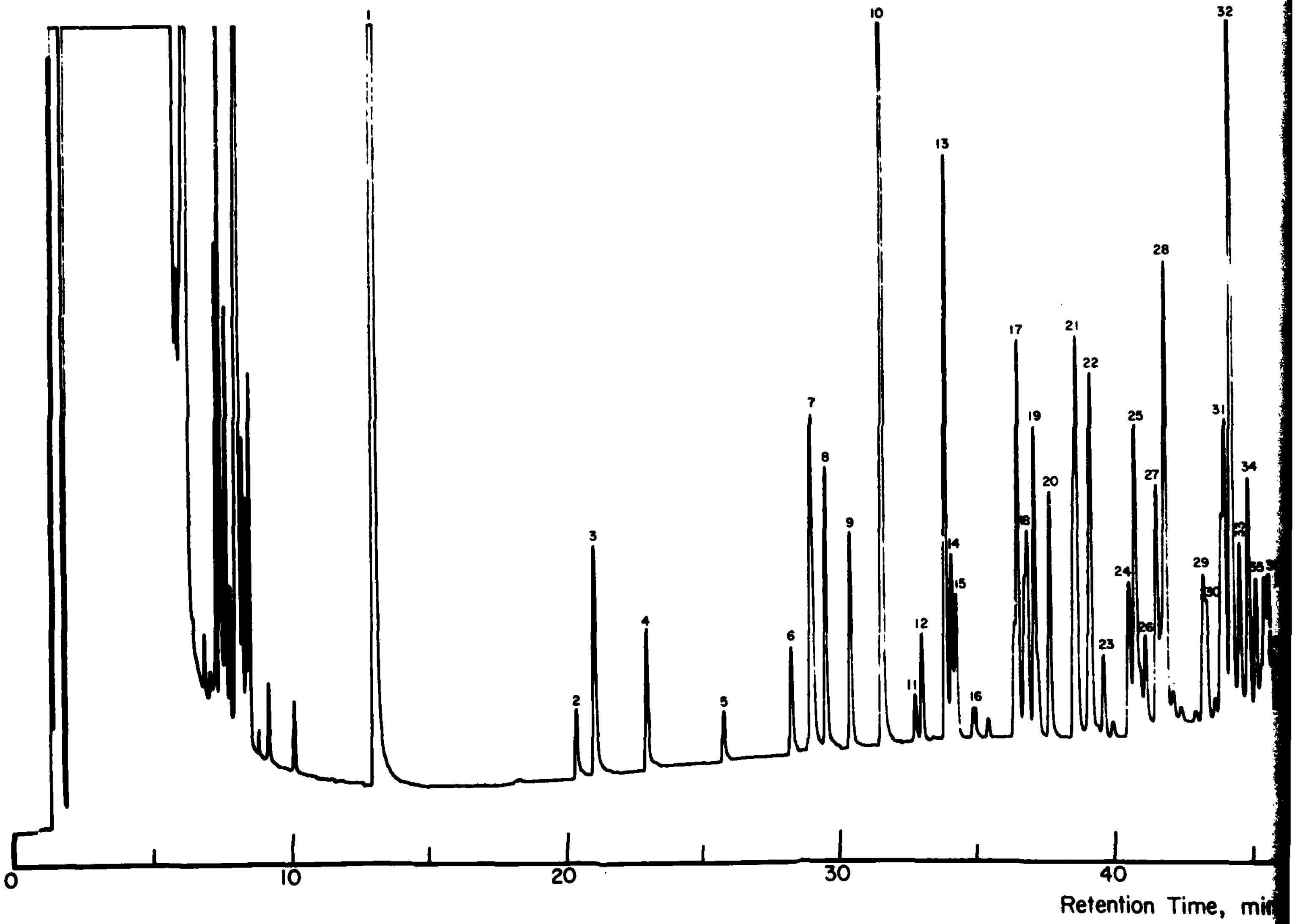
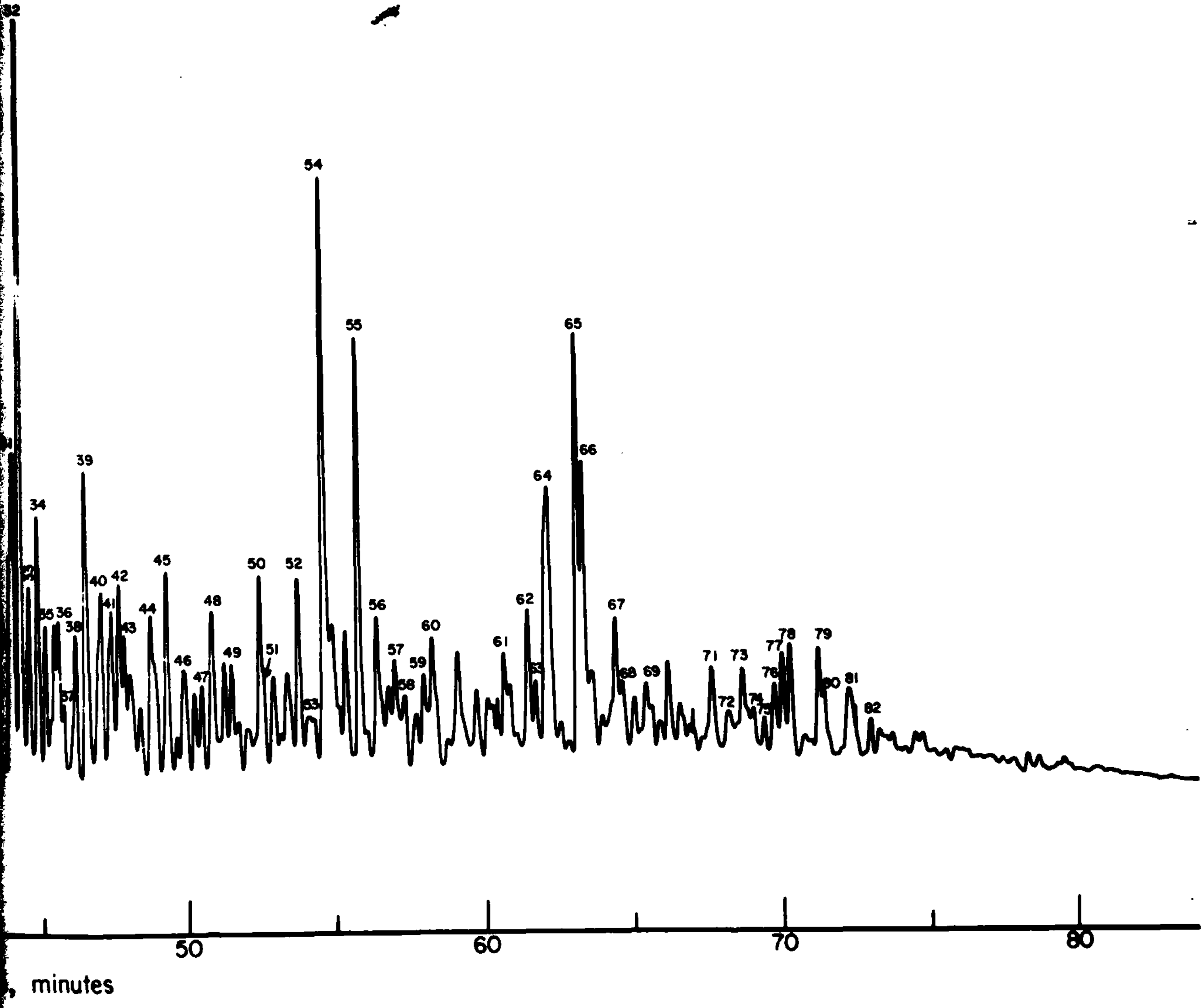


FIGURE 6. FID GAS CHROMATOGRAM



GRAM OF SPECIFICATION JP-8

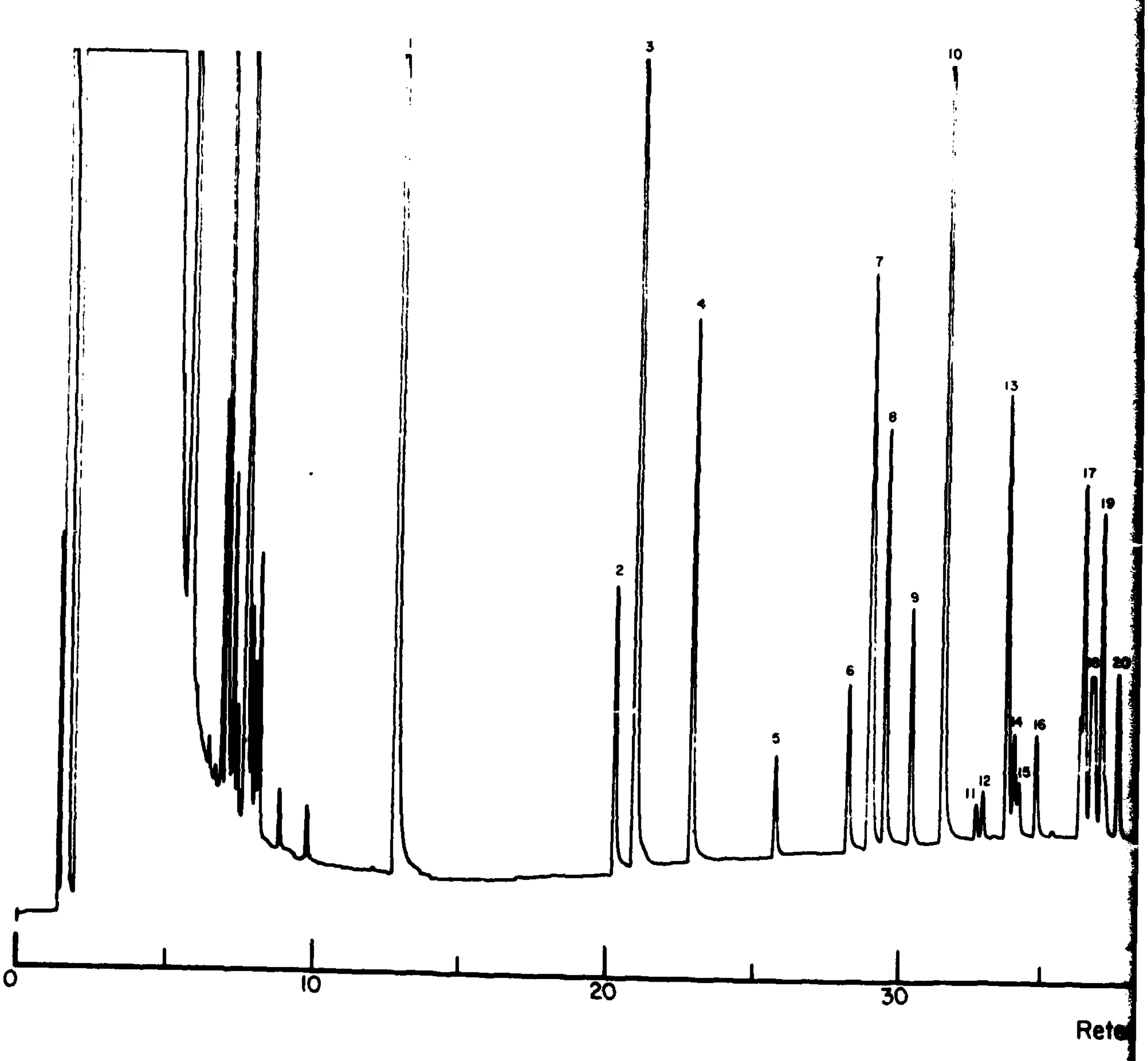
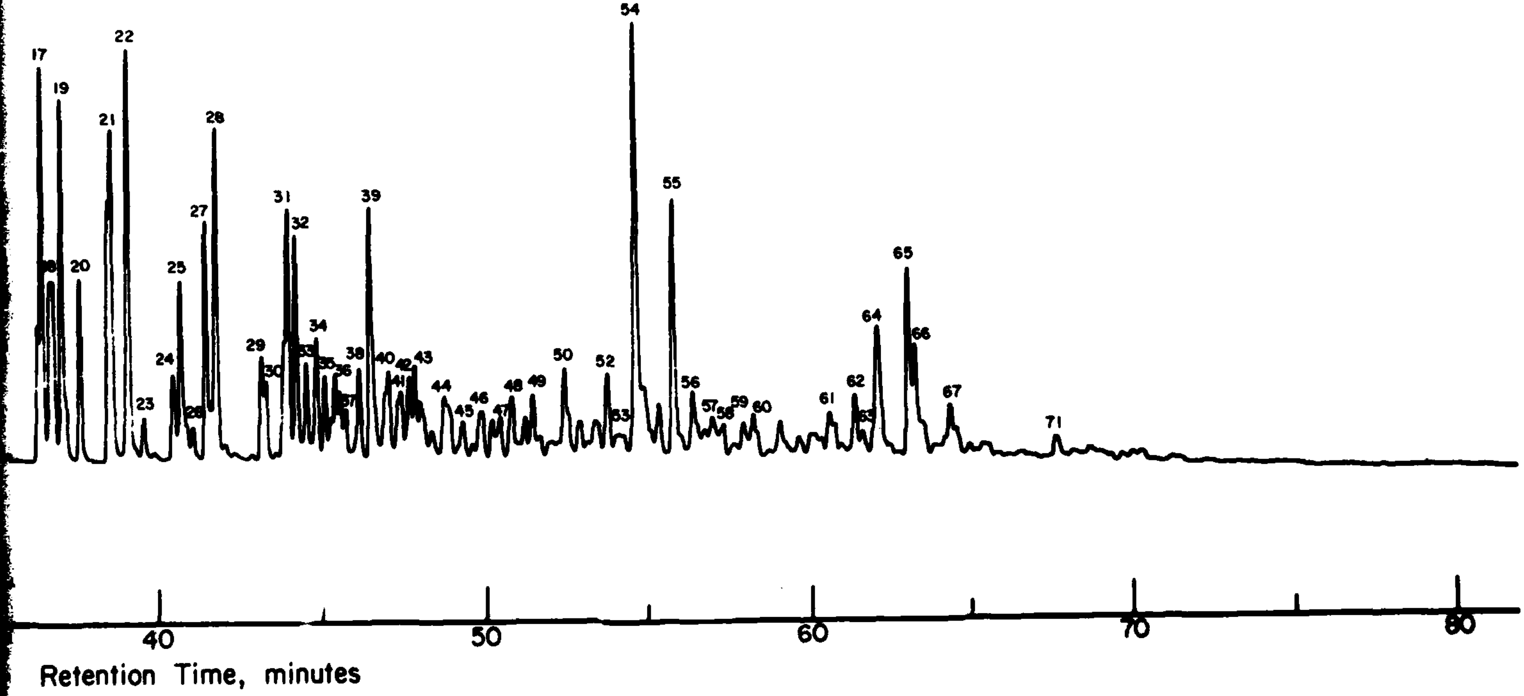


FIGURE 5. FID GAS



GAS CHROMATOGRAM OF SPECIFICATION JP-4

2

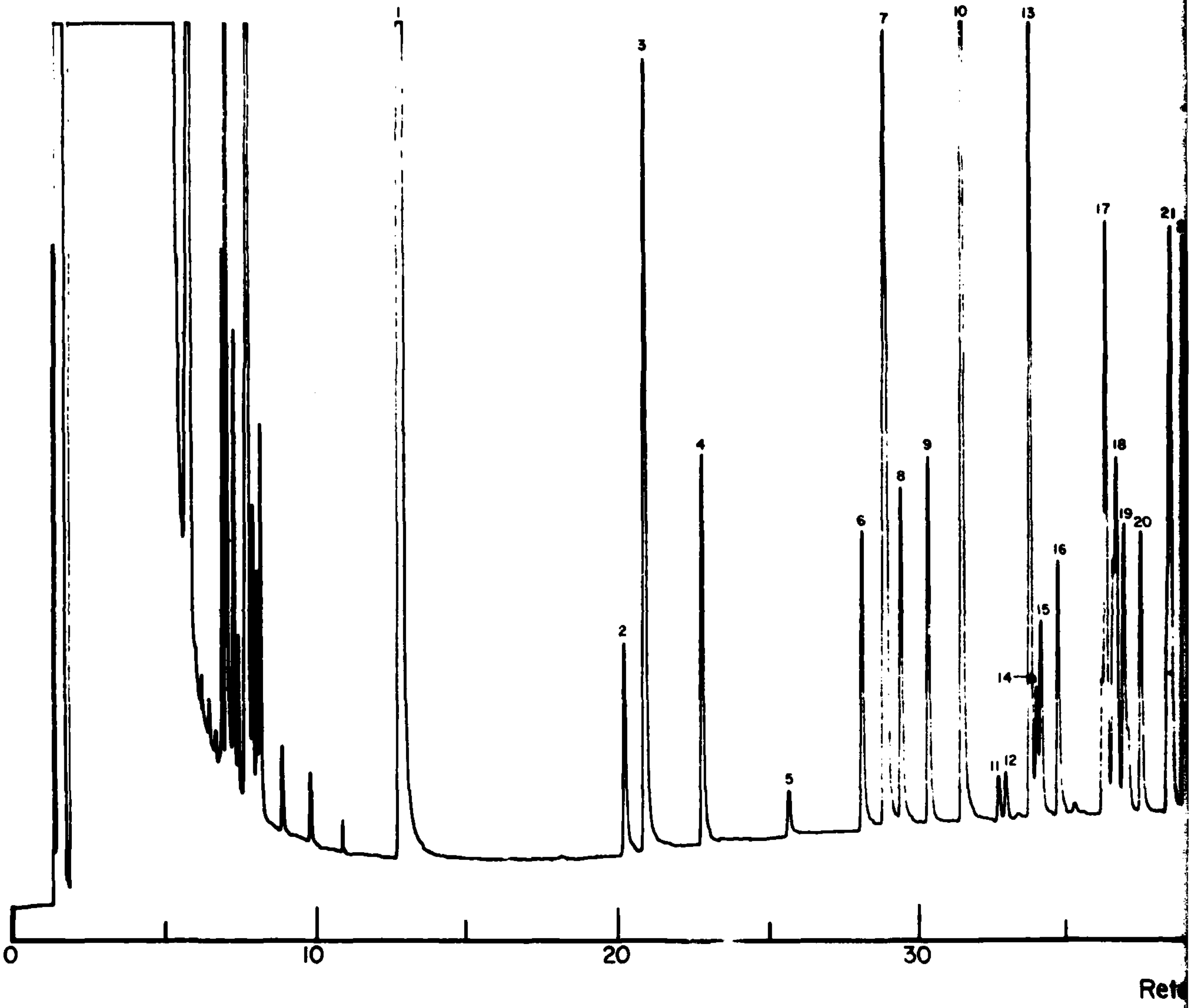
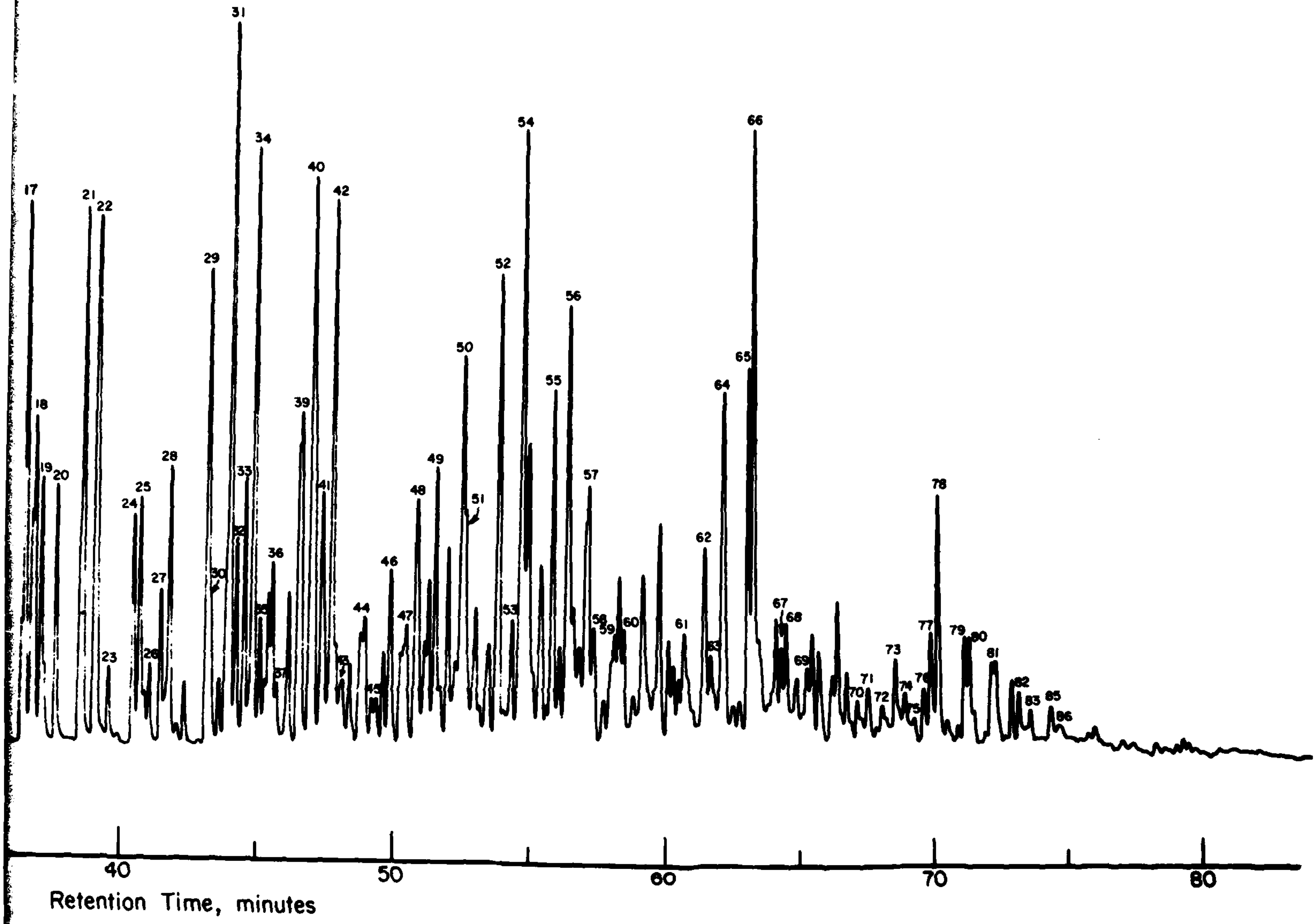


FIGURE 7. FID GAS



D GAS CHROMATOGRAM OF SYNCRUDE JET-A

2

1

TABLE 1. TENTATIVE IDENTIFICATION OF AROMATIC HYDROCARBONS IN JET FUELS

GC Peak No.	Tentative Identification
1.	Toluene
2.	Ethylbenzene
3.	m & p-Xylene
4.	o-Xylene
5.	Isopropylbenzene
6.	Propylbenzene
7.	1-Ethyl-3-methylbenzene & 1-Ethyl-4-methylbenzene
8.	1,3,5-Trimethylbenzene
9.	1-Ethyl-2-methylbenzene
10.	1,2,4-Trimethylbenzene
11.	Isobutylbenzene
12.	sec-Butylbenzene
13.	1,2,3-Trimethylbenzene
14.	1-Methyl-4-isopropylbenzene
15.	1-Methyl-2-isopropylbenzene
16.	Indane
17.	1-Methyl-3-propylbenzene
18.	1-Methyl-4-propylbenzene
19.	1,3-Dimethyl-5-ethylbenzene
20.	1-Methyl-2-propylbenzene
21.	1,4-Dimethyl-2-ethylbenzene
22.	1,3-Dimethyl-4-ethylbenzene
23.	1,2-Dimethyl-4-ethylbenzene & 1,3-Dimethyl-2-ethylbenzene
24.	C_5-Benzene
25.	C_5-Benzene
26.	C_5-Benzene
27.	1,2-Dimethyl-3-ethylbenzene
28.	1,2,4,5-Tetramethylbenzene & 1,2,3,5-Tetramethylbenzene
29.	Methylindane
30.	C_5-Benzene
31.	C_5-Benzene
32.	1,2,3,4-Tetramethylbenzene
33.	C_5-Benzene
34.	C_5-Benzene
35.	C_5-Benzene
36.	C_5-Benzene
37.	C_5-Benzene
38.	C_5-Benzene
39.	Naphthalene
40.	C_5-Benzene
41.	C_5-Benzene
42.	C_5-Benzene
43.	C_5-Benzene
44.	C_5-Benzene
45.	C_5-Benzene
46.	C_6-Benzene
47.	C_5-Benzene
48.	C_6-Benzene
49.	C_2-Indane
50.	C_2-Indane
51.	C_2-Indane
52.	C_2-Indane & C_5-Benzene
53.	C_6-Benzene
54.	2-Methylnaphthalene
55.	1-Methylnaphthalene
56.	C_6-Benzene
57.	C_4-Indane
58.	C_3-Indane
59.	C_3-Indane
60.	C_3-Indane
61.	Biphenyl
62.	2-Ethylnaphthalene
63.	1-Ethylnaphthalene
64.	2,6-Dimethylnaphthalene & 2,7-Dimethylnaphthalene
65.	1,3-Dimethylnaphthalene
66.	1,6-Dimethylnaphthalene
67.	2,3-Dimethylnaphthalene
68.	1,4-Dimethylnaphthalene
69.	1,2-Dimethylnaphthalene
70.	Acenaphthene
71.	Methylbiphenyl
72.	C_3-Naphthalene
73.	C_3-Naphthalene
74.	C_3-Naphthalene
75.	C_3-Naphthalene
76.	C_3-Naphthalene
77.	C_3-Naphthalene
78.	C_3-Naphthalene
79.	C_3-Naphthalene
80.	C_3-Naphthalene
81.	C_3-Naphthalene
82.	C_3-Naphthalene
83.	C_2-Biphenyl or Methylacenaphthene

TABLE 1. (Continued)

GC Peak No.	Tentative Identification	GC Peak No.	Tentative Identification
84.	C_2-Biphenyl or Methylacenaphthene	89.	C_4-Naphthalene
		90.	C_4-Naphthalene
85.	C_4-Naphthalene	91.	C_4-Naphthalene
86.	C_2-Biphenyl or Methylacenaphthene	92.	C_4-Naphthalene
		93.	C_3-Biphenyl or C_2-Acenaphthene
87.	C_3-Biphenyl or C_2-Acenaphthene		
88.	C_4-Naphthalene	94.	C_3-Biphenyl or C_2-Acenaphthene

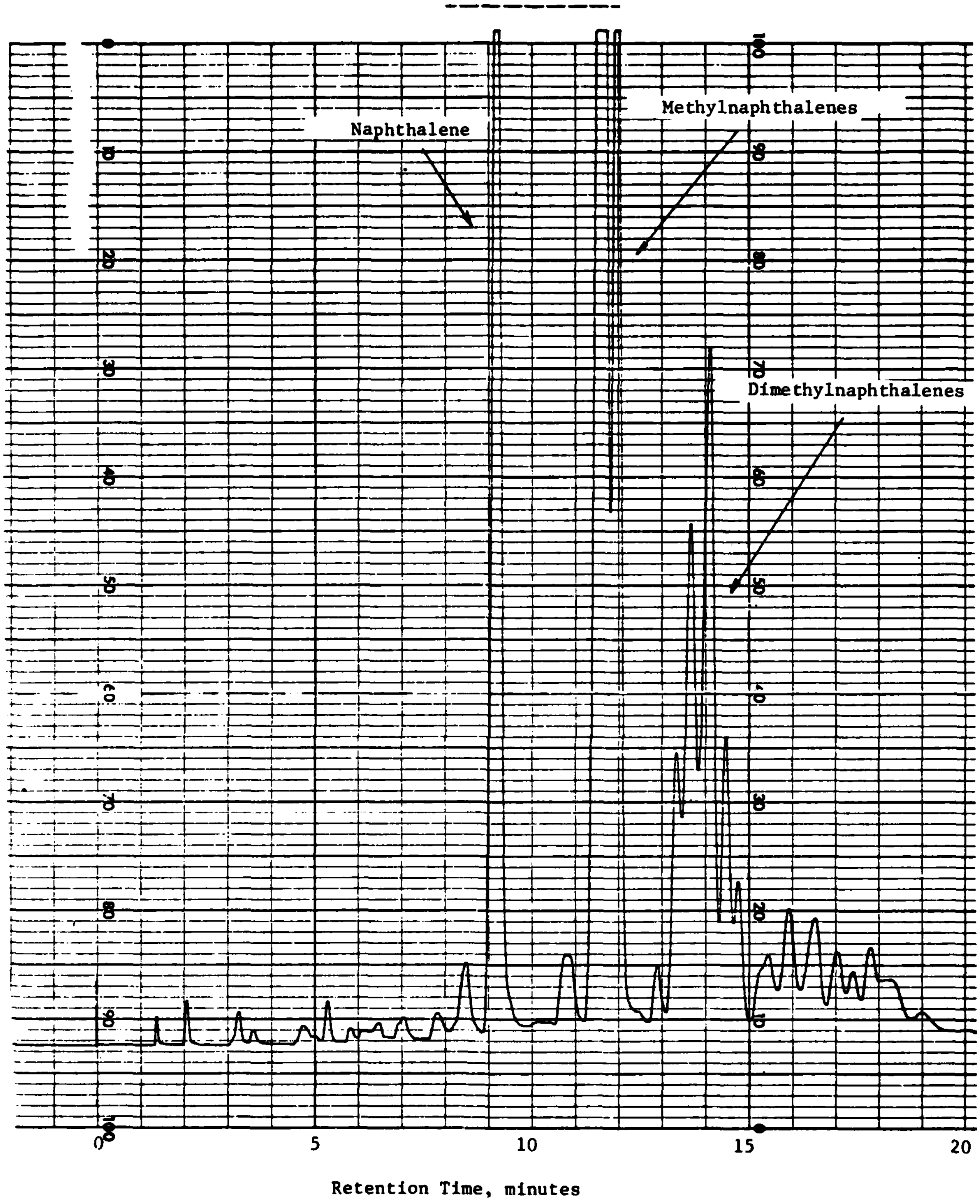


FIGURE 8. PACKED COLUMN GAS CHROMATOGRAM OF PARAHO JP-4 USING UV DETECTOR AT 254 nm.

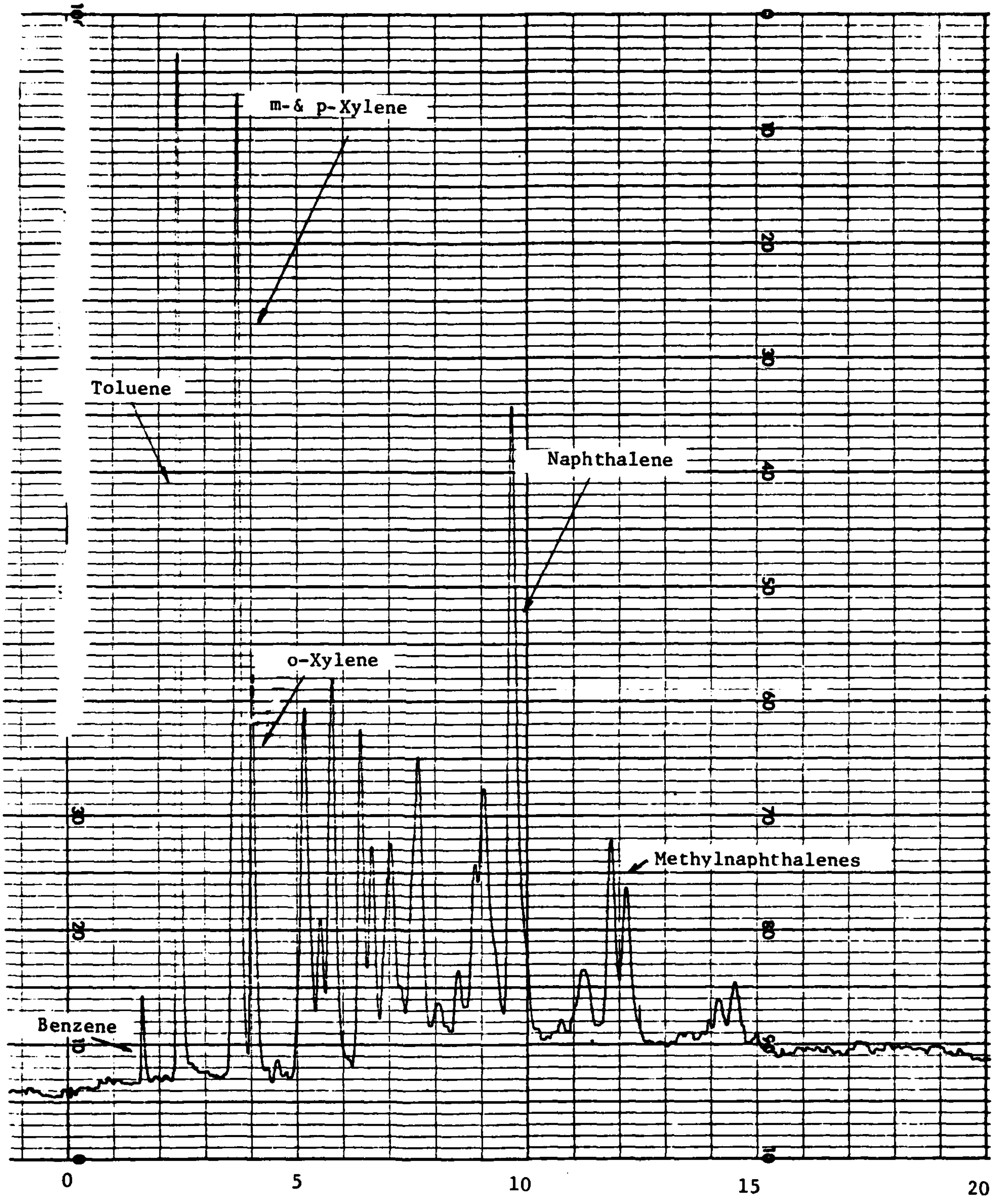


FIGURE 9. PACKED COLUMN GAS CHROMATOGRAM OF SHALE OIL JP-4 USING UV DETECTOR AT 254 nm.

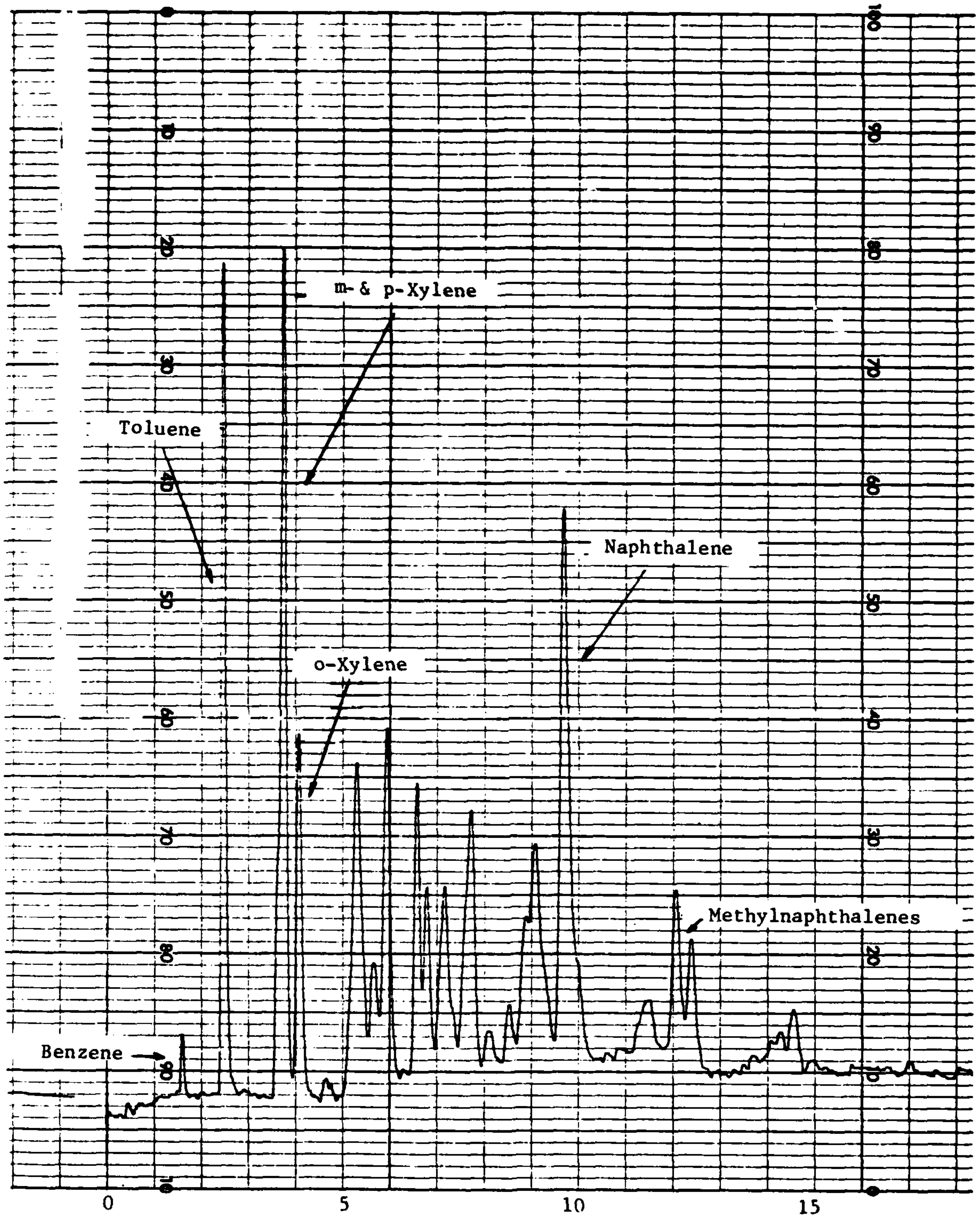


FIGURE 10. PACKED COLUMN GAS CHROMATOGRAM OF SYNCRUDE JP-4 USING UV DETECTOR AT 254 nm.

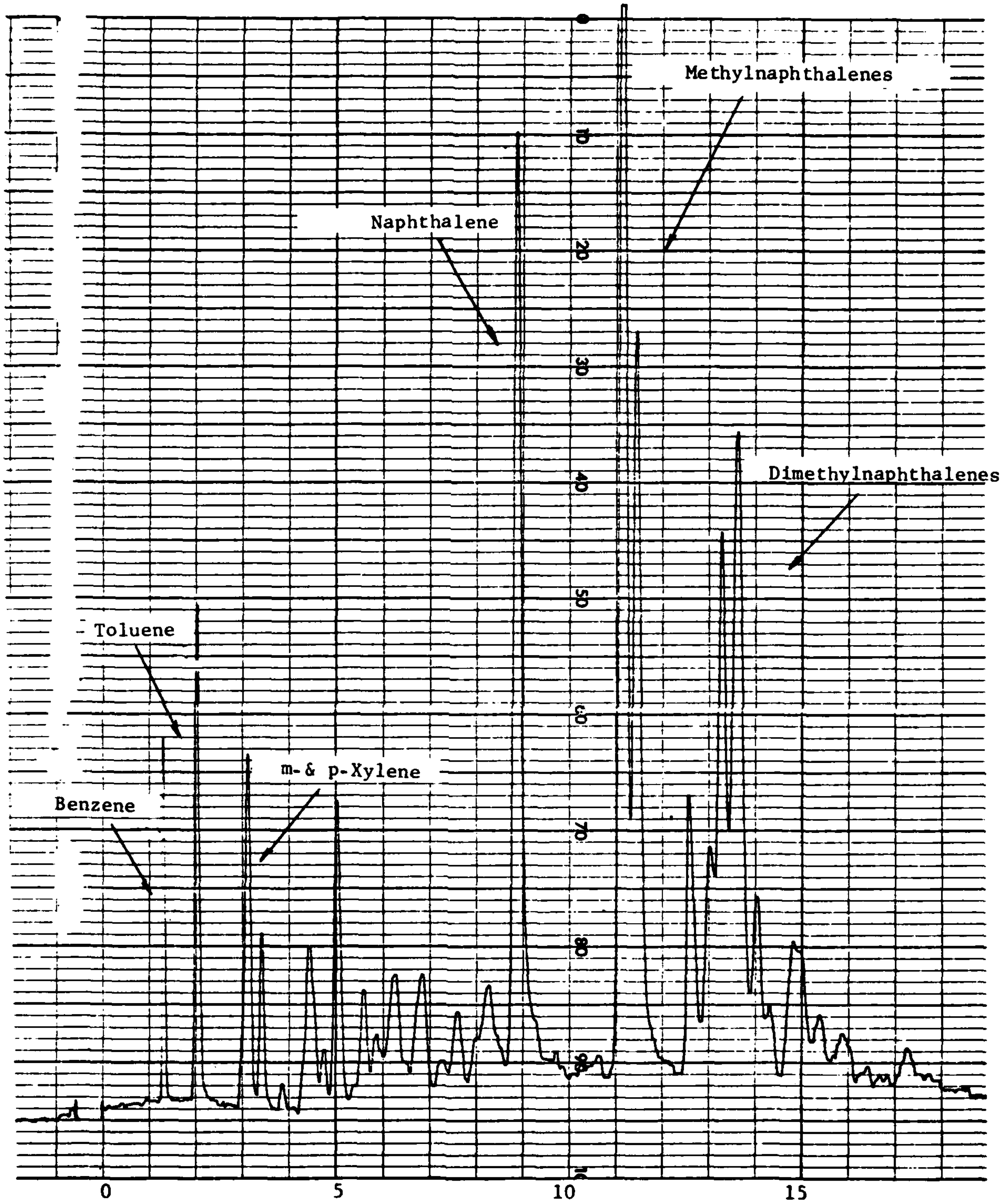


FIGURE 11. PACKED COLUMN GAS CHROMATOGRAM OF SPECIFICATION JP-4 USING UV DETECTOR AT 254 nm.

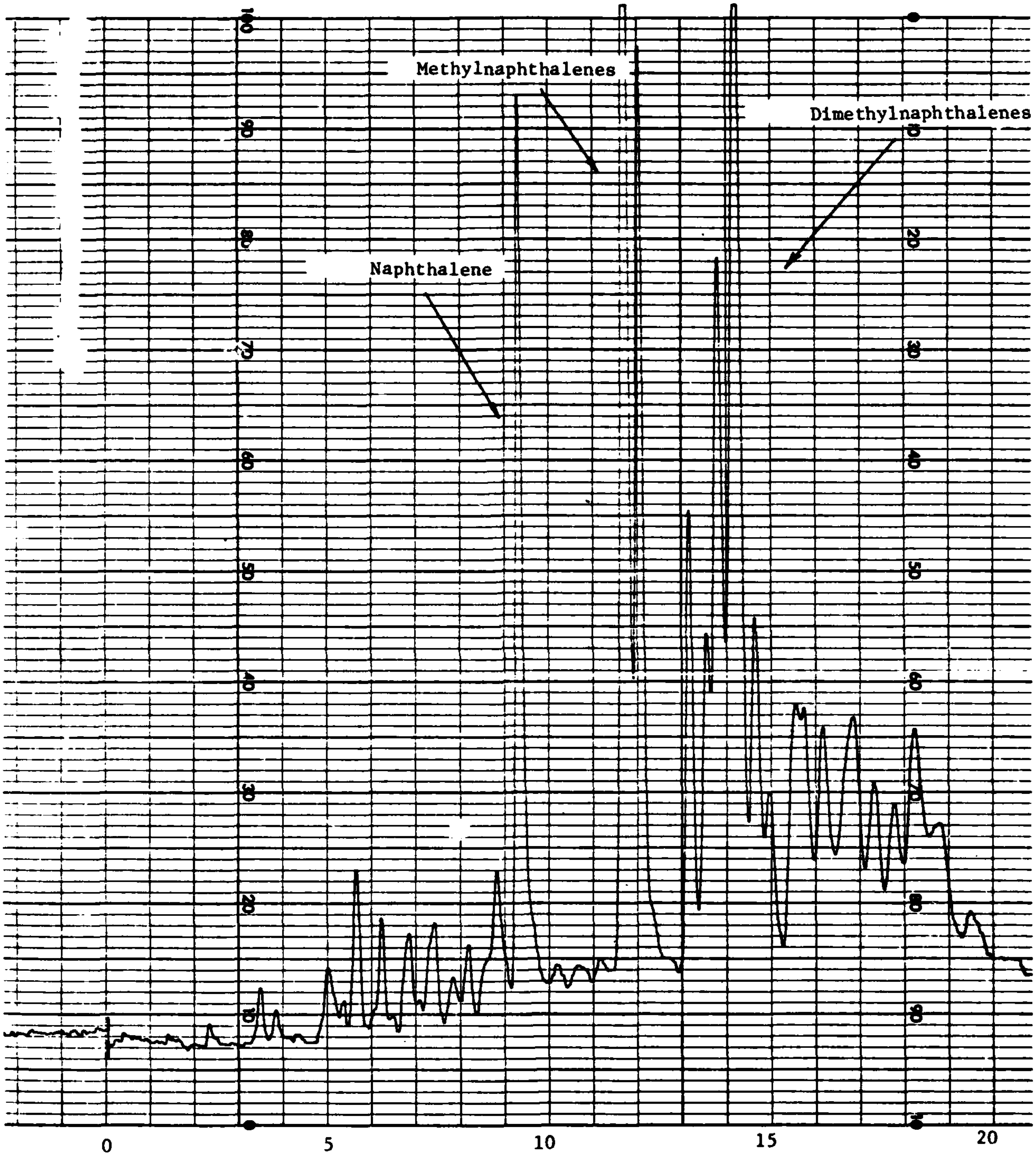


FIGURE 12. PACKED COLUMN GAS CHROMATOGRAM OF SPECIFICATION JP-8 USING UV DETECTOR AT 254 nm.

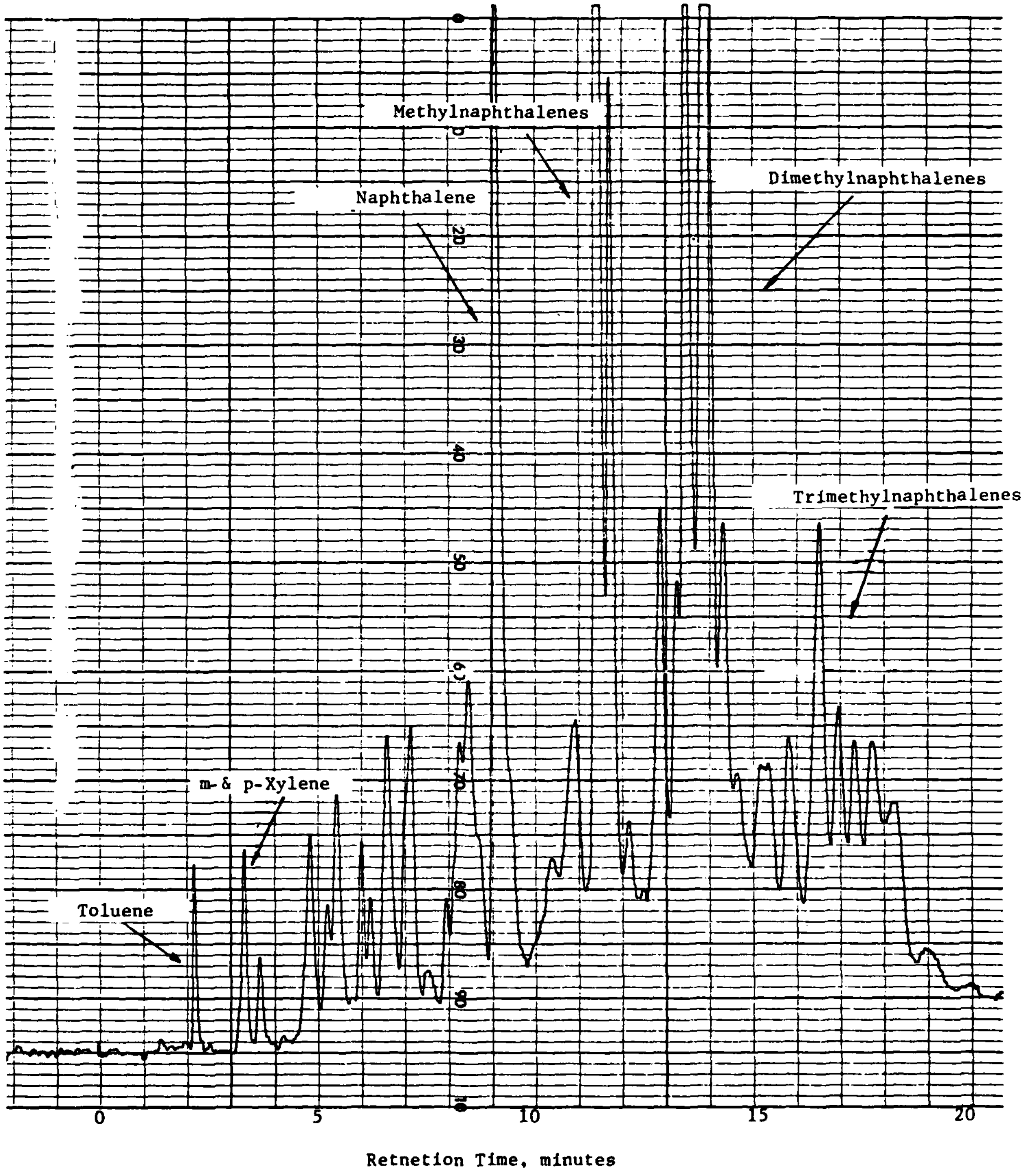


FIGURE 13. PACKED COLUMN GAS CHROMATOGRAM OF SYNCRUDE JET A USING UV DETECTOR AT 254 nm.

shows differences in the relative amounts of some of the major aromatic components. The naphthalene peaks dominate some of the chromatograms because the extinction coefficients for naphthalenes at 254 nm are about ten times greater than those of benzenes.

Comparison of Packed Versus Capillary Column Performance

The major emphasis in the UV detector evaluation was its use with glass capillary column systems. One of the major problems of concern was how to achieve sufficient sensitivity without overloading the column. As indicated above the detection limit for an alkylbenzene using a packed column and the UV detector at 254 nm was about 500 ng. In using capillary column systems however the amount of a single component injected onto the column must generally be kept below about 100 ng in order to prevent overloading and the associated peak broadening. Thus in order to use the UV detector with a capillary column system without overloading the column a much lower detection limit was needed. This could be achieved in part by decreasing the peak width by greater column efficiency and by decreasing the dilution of the column effluent by a lower flow rate in the detector cell.

Studies were carried out to determine the effect of injected amount on peak width and thus determine the extent of overloading using both packed and capillary columns. The UV response was also determined. A capillary column-FID system known to give high column efficiency was compared with the capillary column-UVD system. The peak widths obtained by injecting toluene, o-xylene, and naphthalene are given in Table 2. No evidence of column overloading as indicated by greater peak widths from the higher injected amounts was noted with the capillary-UVD system except when naphthalene was injected. However the FID peak widths clearly showed that overloading occurred at the two highest levels. Apparently dead volume and adsorption in the transfer line, detector, or connectors prevented the full resolution potential of the capillary column from being achieved. Nevertheless, a significant decrease in peak width and increase in UVD sensitivity was achieved by using a capillary column instead of a packed column. The results of a limited comparison of UVD response using the two systems are given in Table 3. They indicate that a 4 to 5-fold increase in sensitivity was achieved with the capillary system. As will be described subsequently, a further increase in sensitivity was achieved by eliminating some of the dead volume in the transfer line connections.

TABLE 2. PEAK WIDTHS USING DIFFERENT GC SYSTEMS

		Peak Width for Given System, Seconds[a]		
Compound	Amount Injected, μg	UVD[b] Packed Column[b]	UVD[b] Cap. Column[d]	FID Cap. Column
Toluene	20	4.8	3.6	2.1
(RT=32. min)	2	5.4	3.6	0.9
	0.2	--	3.6	0.9
	0.02	--	--	--
o-Xylene	20	7.2	3.9	6.3
(RT=42. min)	2	8.4	3.9	2.7
	0.2	--	3.9	1.2
	0.02	--	--	1.5
Naphthalene	20	10.8	8.4	12.6
(RT=9.7 min)	2	9.6	4.8	4.2
	0.2	--	4.2	2.4
	0.02	--	--	2.4

a. Width at half height

b. 254 nm

c. 10'x1/4" x 2 mm I.D. glass column packed with 3% OV-101 on Gas Chrom Q; Helium carrier gas flow rate was 30 ml/min.

d. 30 m x 0.25 mm I.D. WCOT glass column coated with SE-30 (Supelco No. 2-3712). Helium carrier gas flow rate was approx. 1.2 ml/min. Split ratio = 10:1.

Effect of Wavelength on UVD Response

One approach to increasing the response obtained from the UVD for aromatic hydrocarbons involves operation at a wavelength at which the compounds have higher extinction coefficients. The ultraviolet spectra of 1,2,4-trimethylbenzene and naphthalene in hexane, given in Figures 14 and 15, respectively, are representative of the spectra of aromatic components expected in jet fuels. The spectra show that although the extinction coefficients at 254 nm are higher than they are at 235 or 300 nm they are not as high as they are at 200 to 220 nm. For 1,2,4-trimethylbenzene the extinction coefficient increases from 320 at 262 nm to 8,800 at 214 nm, an increase of over 25-fold. For naphthalene the extinction coefficient increases from 3,450 at 258 nm to 117,000 at 221 nm, an increase of over 30-fold.

The capillary column GC-UVD system was evaluated at 220 nm and 208 nm using aromatic hydrocarbon standards. The results, given in Table 4, show that a slight improvement in sensitivity was obtained by operating at 220 nm instead of 254 nm but a much greater improvement was achieved at 208nm. It thus appears that the absorption maxima in the gas phase are shifted to lower wavelength relative to those in solution. It was of particular interest to note that even at 208 nm no response was obtained from the hexane solvent thus indicating that the UVD is highly selective for aromatic hydrocarbons even at the low wavelength.

Capillary Column - UVD Interface

Despite the fact that the manufacturer recommends the use of makeup gas when the UVD is used with a capillary system, the capillary column - UVD studies described above were performed without makeup gas. The capillary column was connected to the system with provision for makeup gas, but as the makeup gas was progressively decreased from 30 ml/min to none at all the UVD response gradually increased. This result is as expected since the UVD is effluent-concentration dependent, and makeup gas dilutes the column effluent. Apparently any increase in response due to peak narrowing resulting from makeup gas is not enough to counteract the decrease in response due to dilution.

1,2,4-Trimethylbenzene (Pseudocumene) 1,2,4-Trimethylbenzol (Pseudocumol)		02/9 30 000/00.223
Spectrometer Spektrometer Zeiss M40 III, PMQ II (N_2 flushed)	Solvent Lösungsmittel Hexane	Formula Formel C_9H_{12}
Spec. resn Spek. Auflösung 40–50 cm^{-1}	Concn Konz. $1{\cdot}26 \times 10^{-4}$, $1{\cdot}26 \times 10^{-3}$, $1{\cdot}26 \times 10^{-2}$ M	Mol. wt Mol. Gew 120·2 b.p. 169°
Cell length Schichtdicke 0·1, 1·0 cm	Purity Reinheit Dist.	LR 212
G. Vagt, H. Bruns: Inst. org. Chem., Abt. Molekülspektroskopie, T. H. Braunschweig		

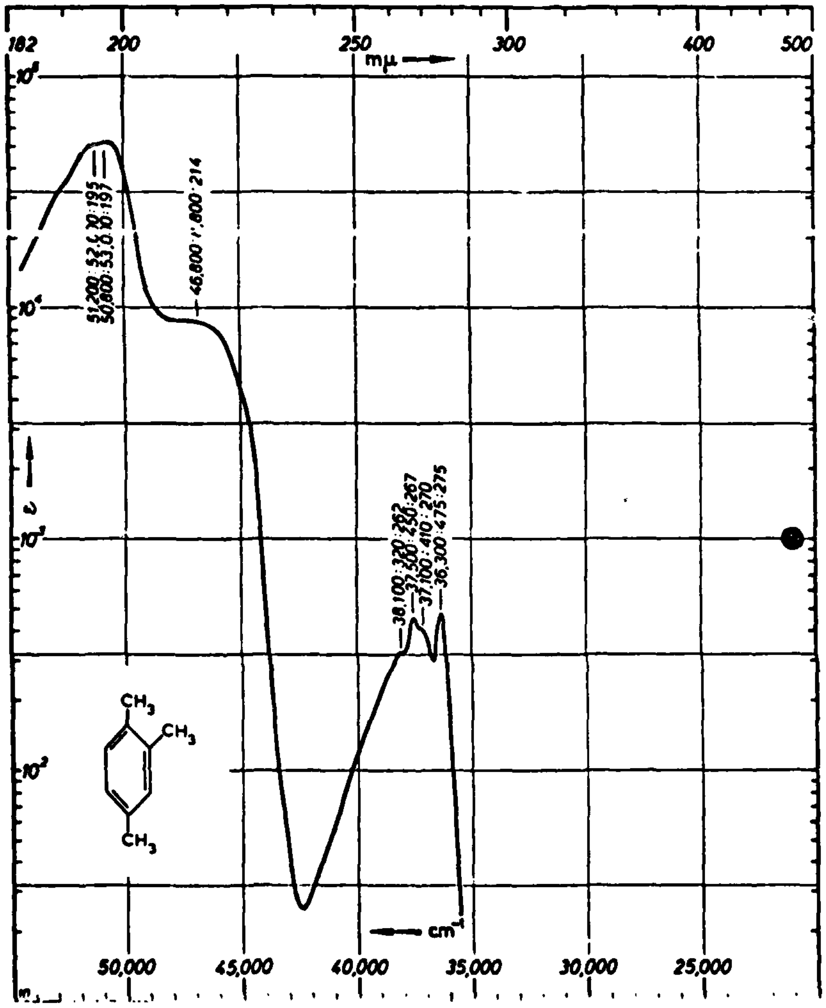


FIGURE 14. UV SPECTRUM OF 1,2,4-TRIMETHYLBENZENE IN HEXANE (From UV ATLAS of Organic Compounds, Plenum Press, N.Y.)

Naphthalene Naphthalin		E 1/1 32.000/00.600
Spectrometer Spektrometer Cary 11, Hilger Uvispek	**Solvent** Lösungsmittel Hexane	**Formula** Formel $C_{10}H_8$
Spec. resn Spek. Auflösung 30 cm^{-1} at 45,200 cm^{-1} 12 cm^{-1} at 36,400 cm^{-1} 11 cm^{-1} at 33,300 cm^{-1}	**Concn** Konz. $5{\cdot}896 \times 10^{-5}$, $1{\cdot}179 \times 10^{-4}$, $2{\cdot}220 \times 10^{-4}$, $2{\cdot}948 \times 10^{-4}$, $5{\cdot}551 \times 10^{-4}$, $1{\cdot}112 \times 10^{-3}$, $5{\cdot}56 \times 10^{-3}$, $1{\cdot}112 \times 10^{-2}$ M	**Mol. wt** Mol. Gew. 128·2 m.p. 80·2°
Cell length Schichtdicke 0·526, 2·0, 5·0 cm	**Purity** Reinheit Zone refined	**LR** ·9021, 9238
E. M. F. Roe: Chester Beatty Res. Inst., Royal Cancer Hospital, London		

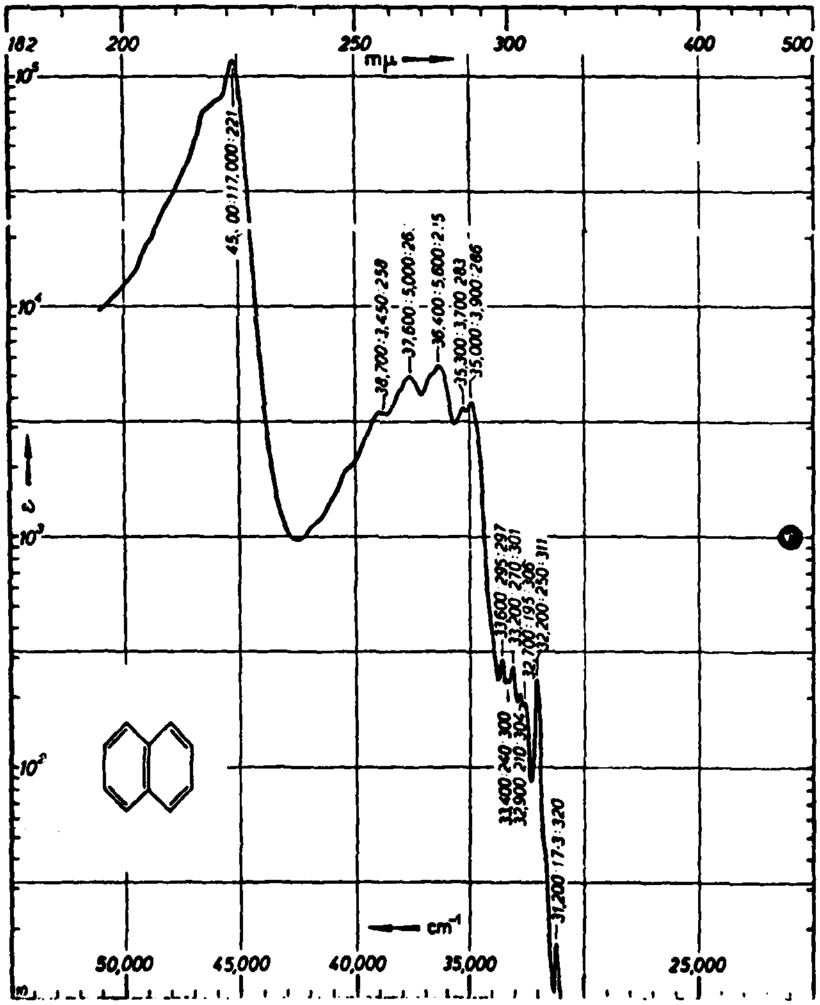


FIGURE 15. UV SPECTRUM OF NAPHTHALENE IN HEXANE (From UV Atlas of Organic Compounds, Plenum Press, N.Y.)

TABLE 3. UVD RESPONSE USING DIFFERENT GC SYSTEMS

Compound	Amount Injected, μg	% Transmittance at 254 nm	
		Packed Column	Capillary Column
Toluene	20	98.0	94.5
	2	99.8	99.4
	0.2	--	99.9
o-Xylene	20	98.7	96.5
	2	99.8	99.4
	0.2	--	100.0
Naphthalene	20	86.6	71.3
	2	98.4	92.0
	0.2	--	99.2

TABLE 4. UVD RESPONSE AT DIFFERENT WAVELENGTHS

Compound	Amount Injected, μg	% Transmittance at Given Wavelength[a]		
		254 nm	220 nm	208 nm
Toluene	0.2	99.9	99.9	98.6
o-Xylene	0.2	100.0	99.7	98.7
Naphthalene	0.2	99.2	97.8	85.1

[a] Using a 30 m x 0.25 mm I.D. WCOT glass capillary column coated with SE-30 (Supelco No. 2-3712). Helium carrier gas flow rate was approx. 1.2 ml/min. Split ratio = 10:1.

The system was further improved by removing the makeup gas tee and replacing it with a low dead-volume union. Calculations of the efficiency of this system indicated that about 35,000 theoretical plates were achieved which compares quite favorably with the 50,000 plates obtained with the same column and injector system using an FID. Other dead volume problems and adsorption problems caused by the stainless steel transfer line in the system probably account for the remaining loss in column efficiency.

The capillary column-UVD system with 35,000 plates was used at 208 nm to analyze the six jet fuels supplied by the sponsor. The fuels were dissolved in petroleum ether to give 0.5 percent solutions and 2 μl was injected with a 10:1 split ratio. A 30m x 0.25 mm I.D. WCOT glass column coated with SE-30 was used for this work. The column temperature was programmed from 80 to 200°C. The chromatograms obtained are given in Figures 16 to 21. The peak number assignments are those given earlier in Table 1. The superior resolution of the glass capillary column system is made dramatically clear by comparing these chromatograms with those obtained with a packed column and shown previously in Figures 8 to 13.

Response Characteristics of Model Compounds

The capillary column-UVD system described above was used to study the response characteristics of five aromatic hydrocarbon reference compounds, namely toluene, o-xylene, 1,2,4-trimethylbenzene(pseudocumene), 1,2,4,5-tetramethylbenzene(durene), and naphthalene. The compounds were dissolved in petroleum ether in concentrations ranging from 0.001% to 1.0% and 2 μl was injected into the system with a split ratio of 10:1.

The response was found to be quite linear in all cases as indicated by a slope of 1.0 for the log-log plots given in Figures 22 to 26. Response factors, determined as response relative to that of pseudocumene, were calculated for toluene, o-xylene, durene, and naphthalene. The data obtained including the standard deviations are given in Table 5. The response factors were generally constant to within about 10% over a concentration range of 0.004% to 1.0%. The response factor for naphthalene was approximately 10-times greater than for the alkylbenzenes.

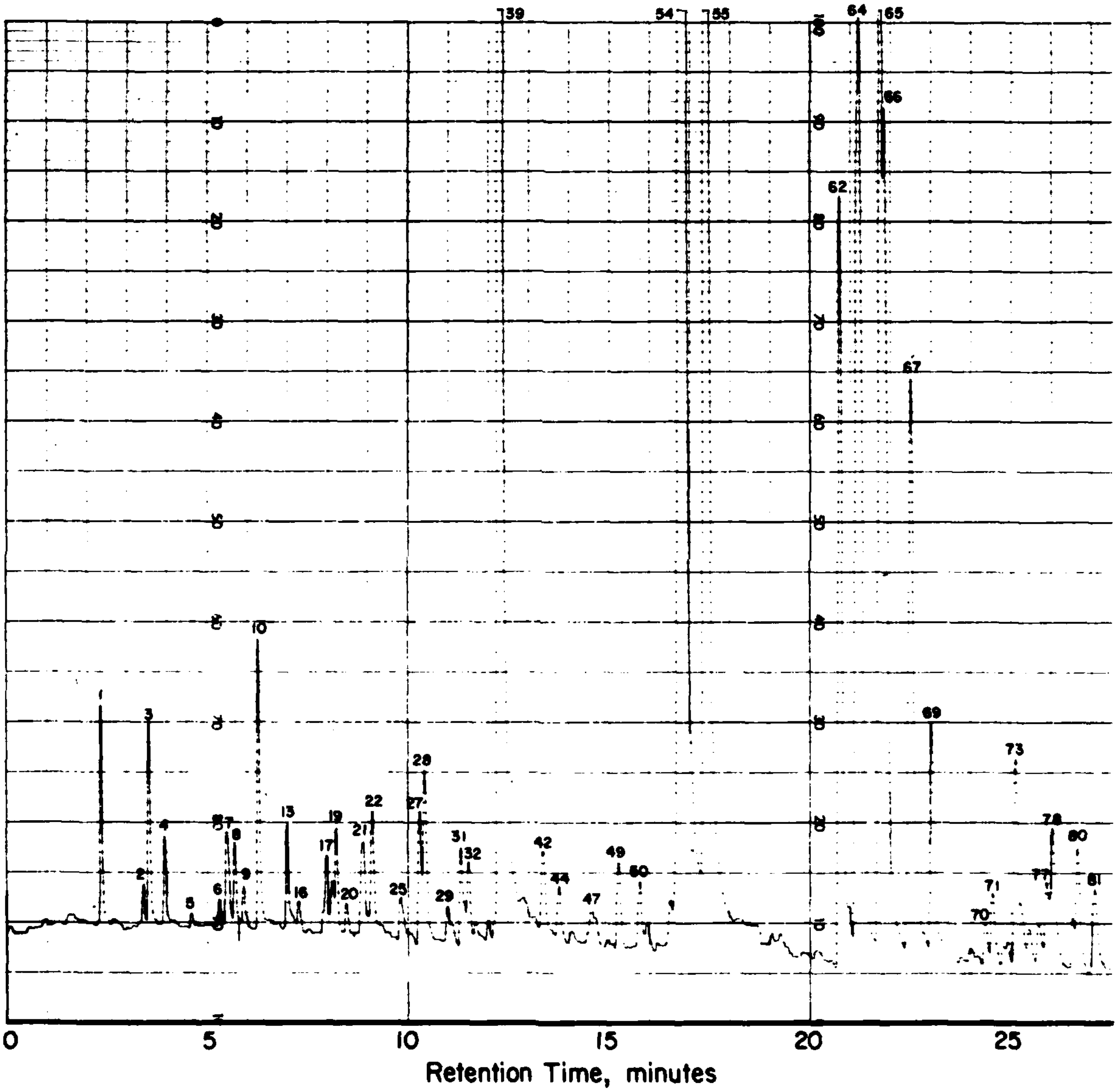


FIGURE 16. CAPILLARY COLUMN GAS CHROMATOGRAM OF PARAHO JP-4 USING UV DETECTOR

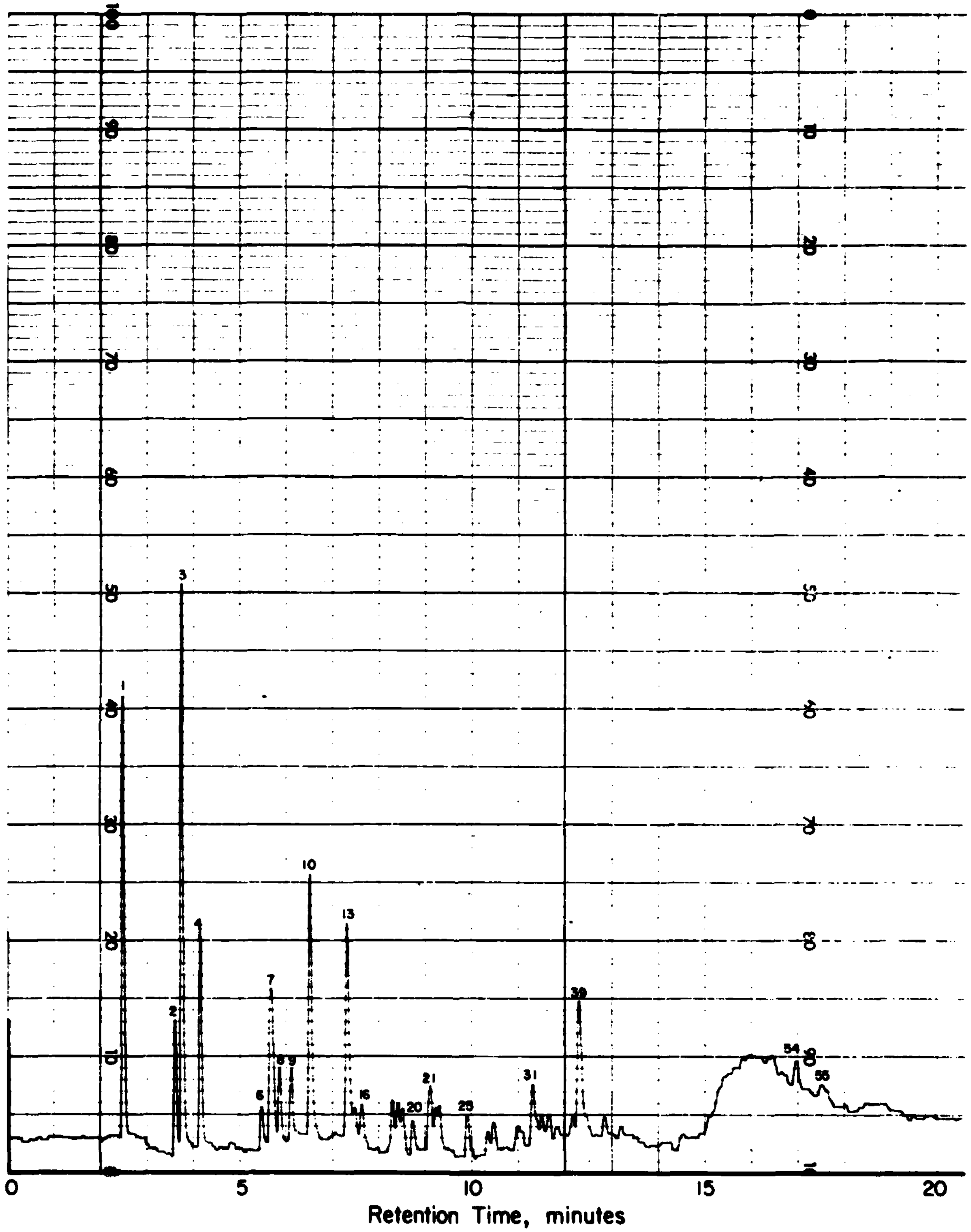


FIGURE 17. CAPILLARY COLUMN GAS CHROMATOGRAM OF SHALE OIL JP-4 USING UV DETECTOR AT 208 nm.

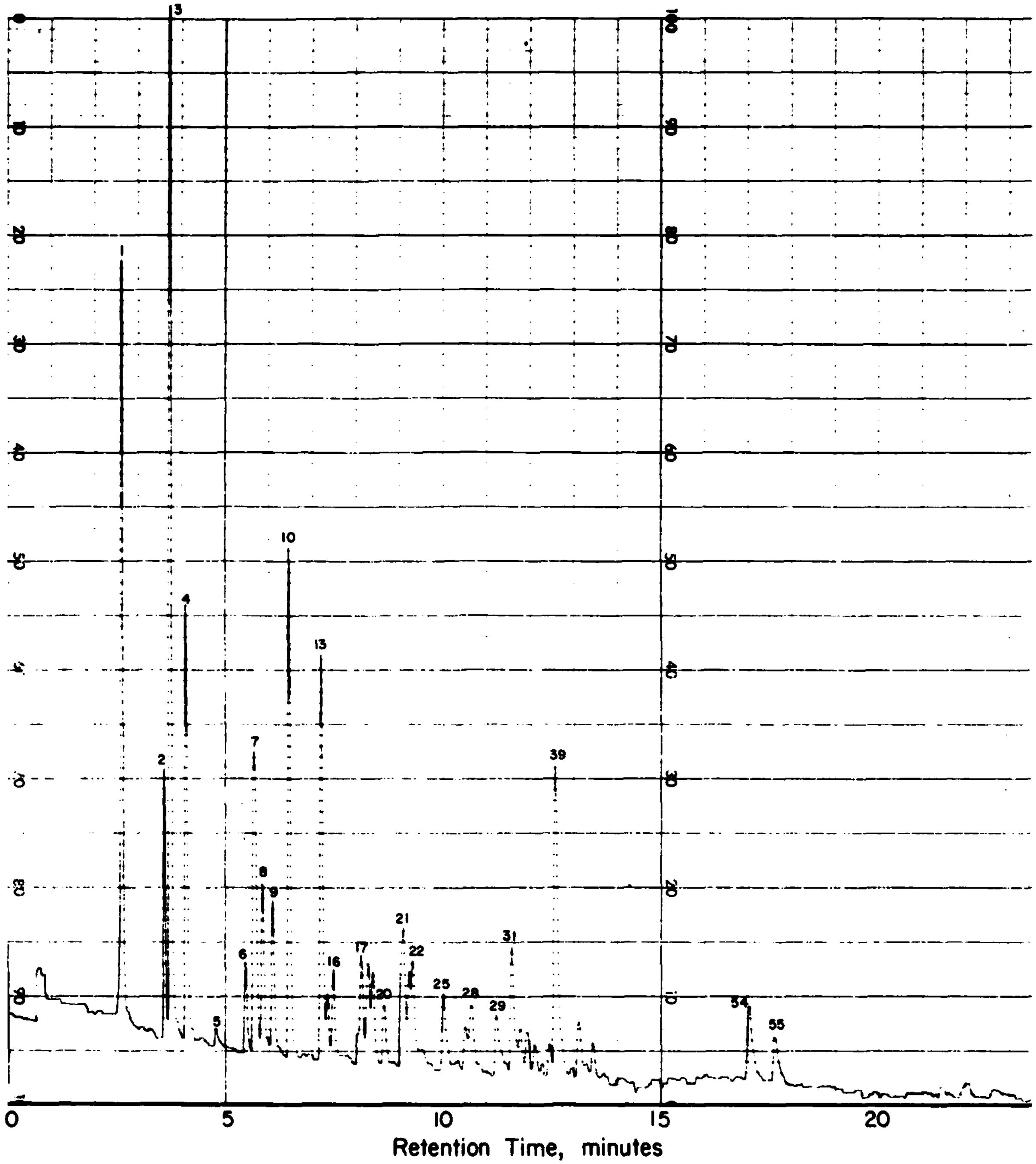


FIGURE 18. CAPILLARY COLUMN GAS CHROMATOGRAM OF SYNCRUDE JP-4 USING UV DETECTOR AT 208 nm.

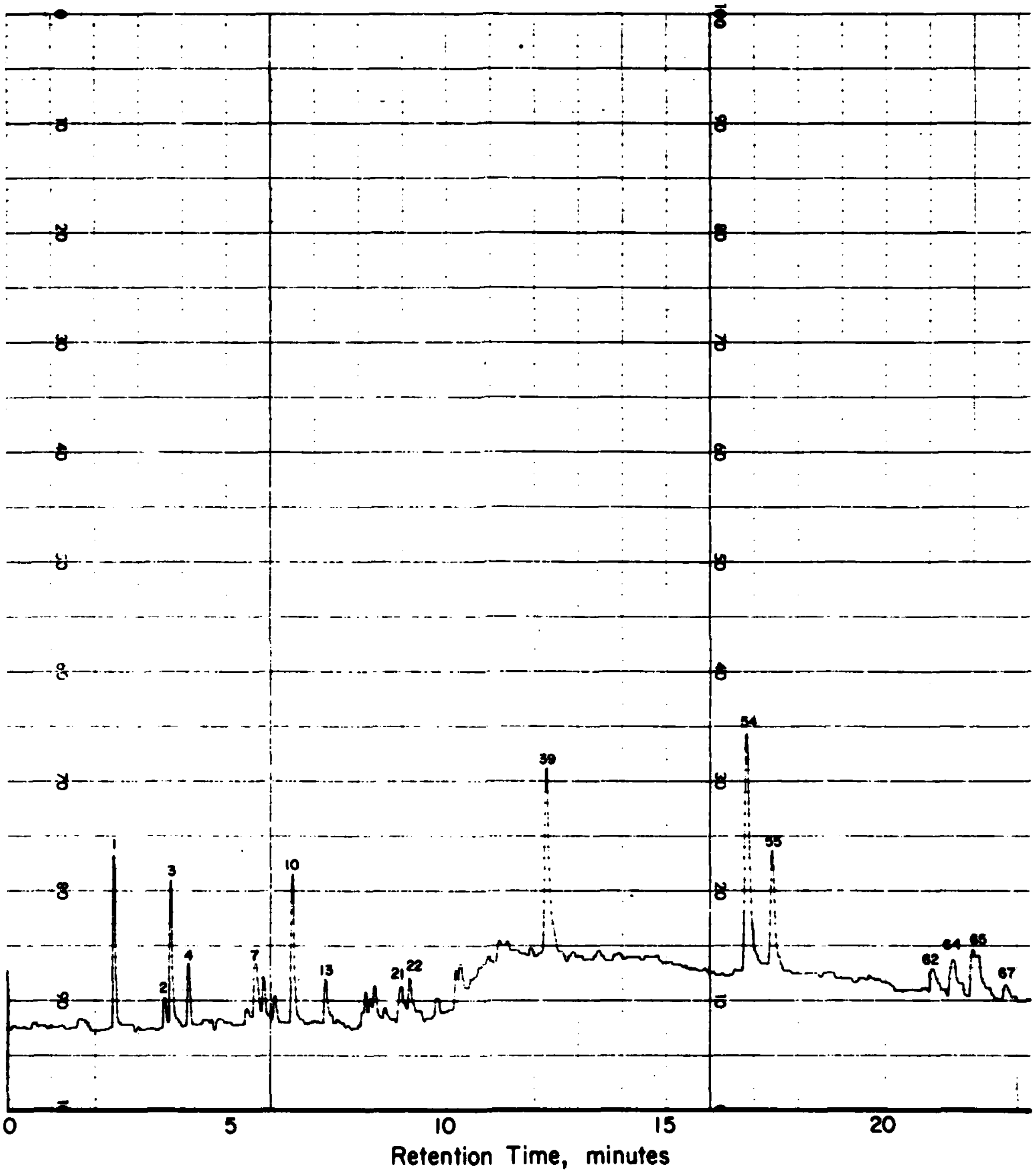


FIGURE 19. CAPILLARY COLUMN GAS CHROMATOGRAM OF SPECIFICATION JP-4 USING UV DETECTOR AT 208 nm.

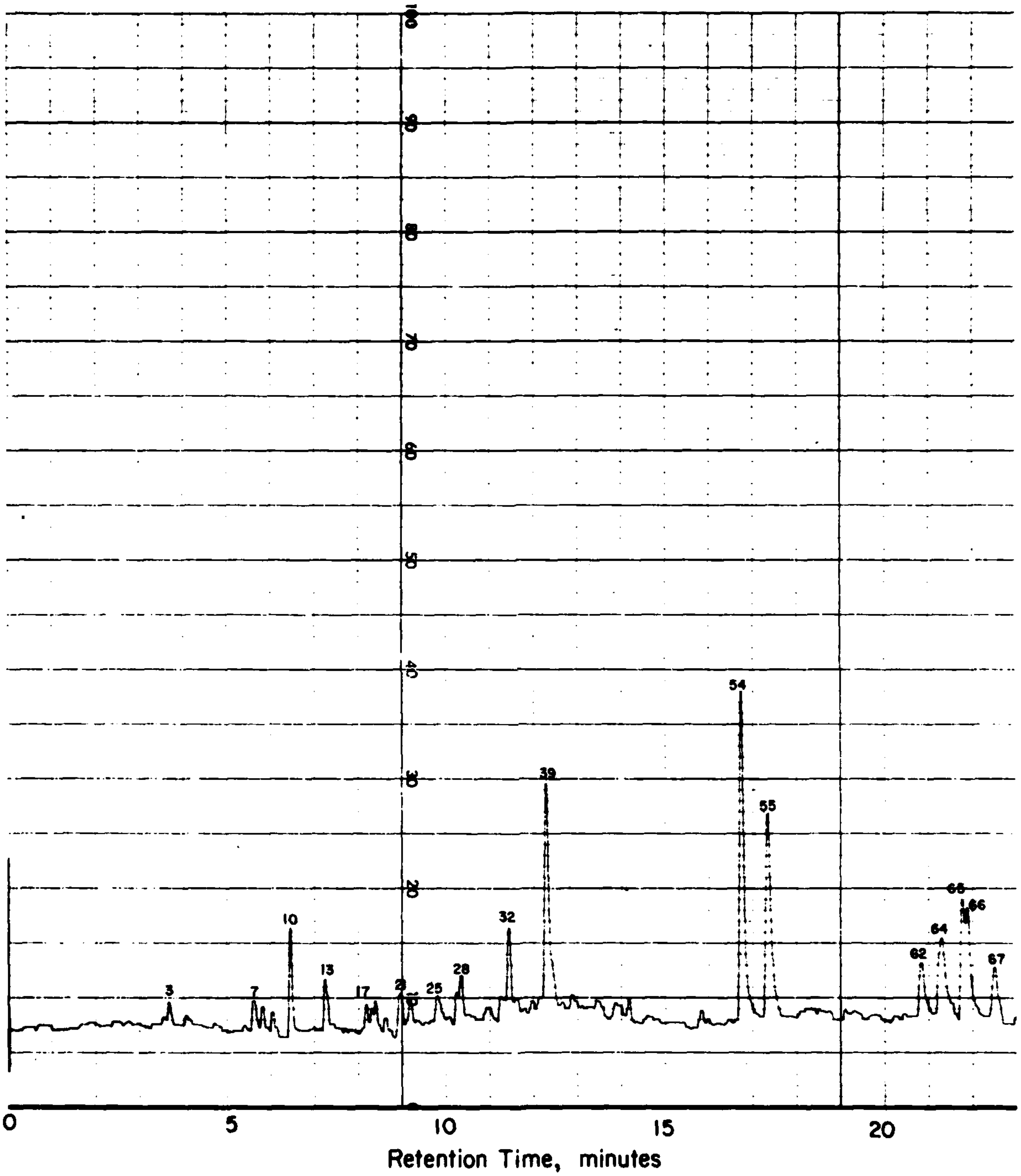


FIGURE 20. CAPILLARY COLUMN GAS CHROMATOGRAM OF SPECIFICATION JP-8 USING UV DETECTOR AT 208 nm.

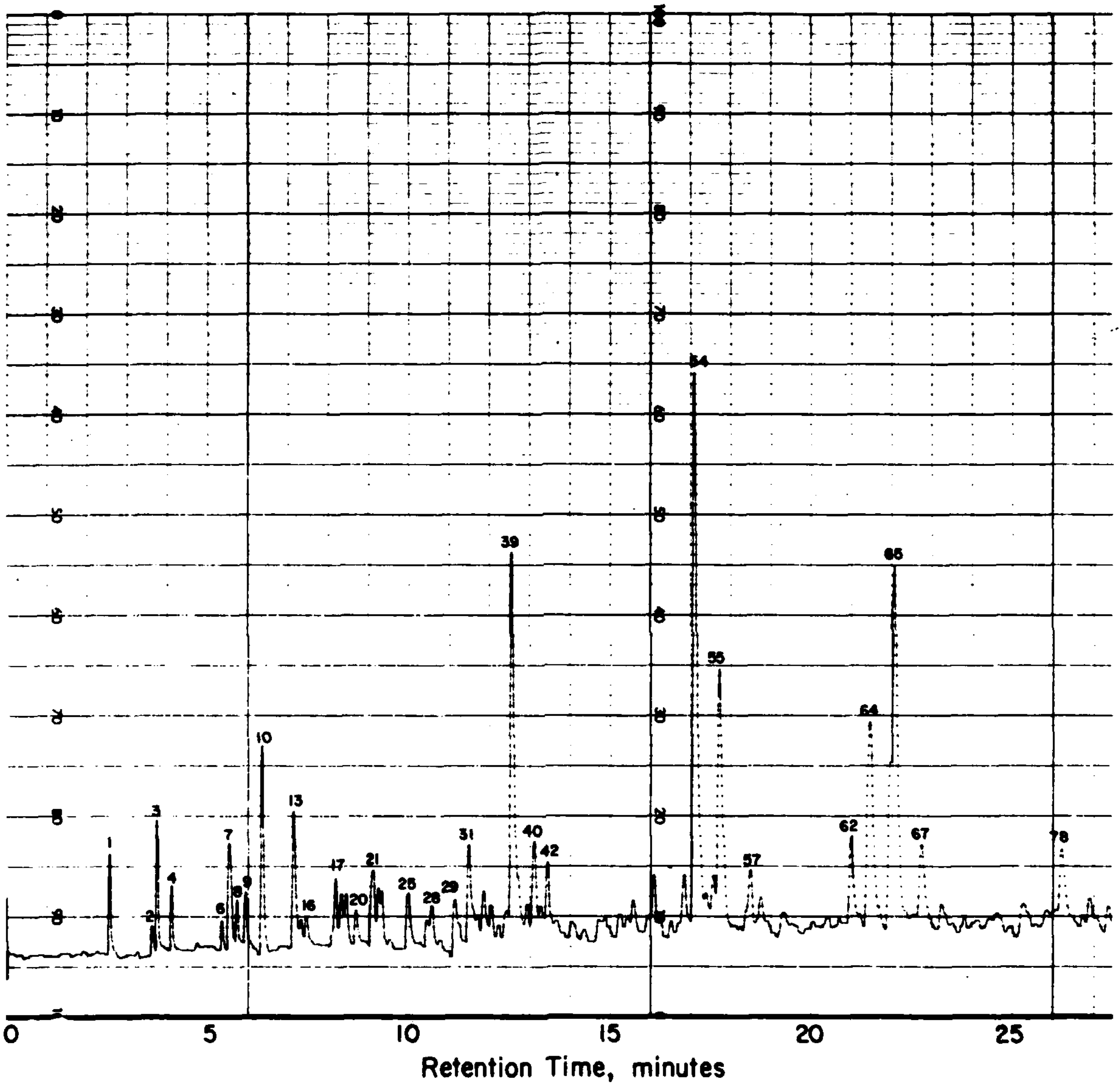


FIGURE 21. CAPILLARY COLUMN GAS CHROMATOGRAM OF SYNCRUDE JET-A USING UV DETECTOR AT 208 nm.

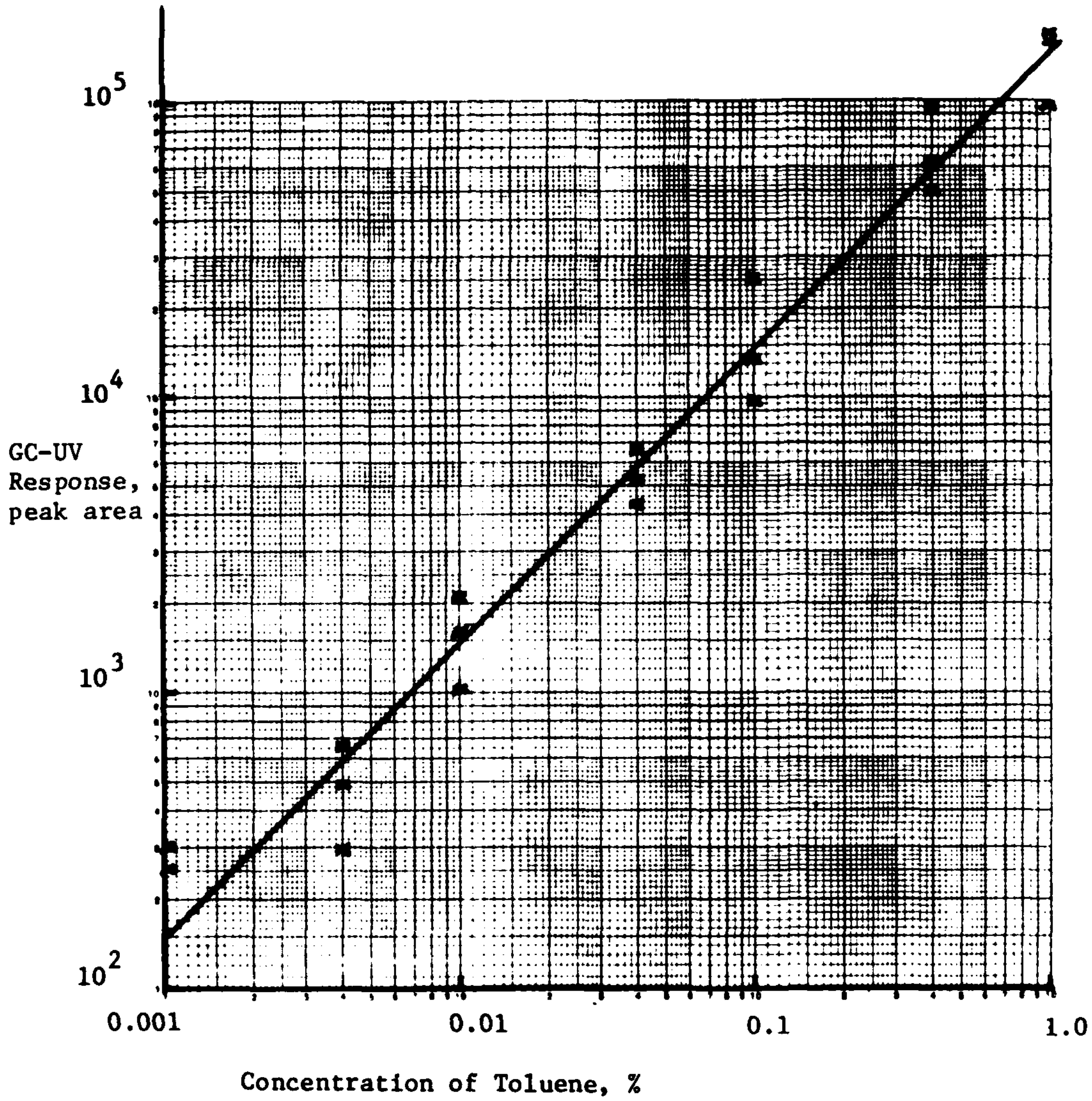


FIGURE 22. GC-UV RESPONSE OF TOLUENE

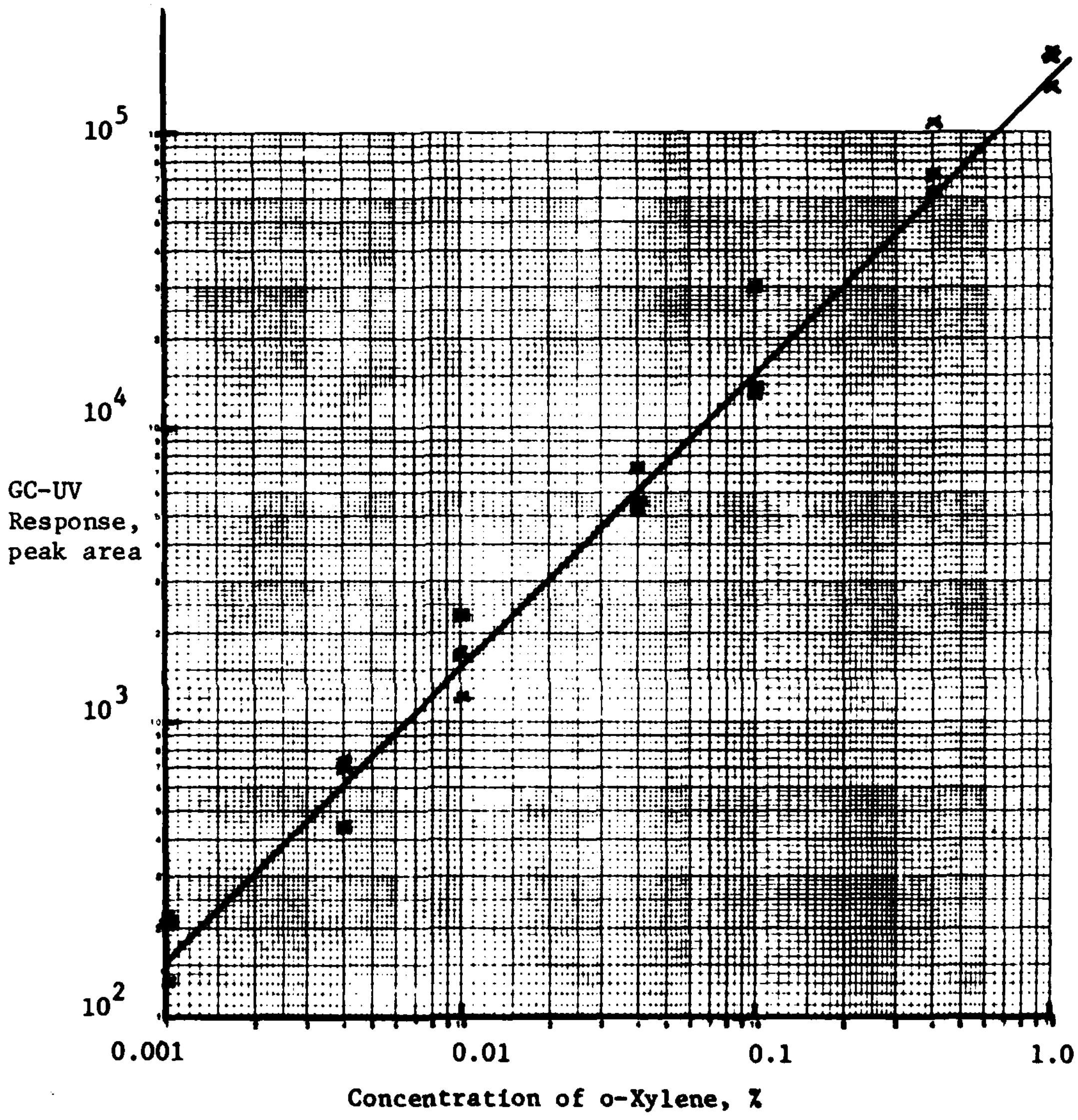


FIGURE 23. GC-UV RESPONSE OF o-XYLENE

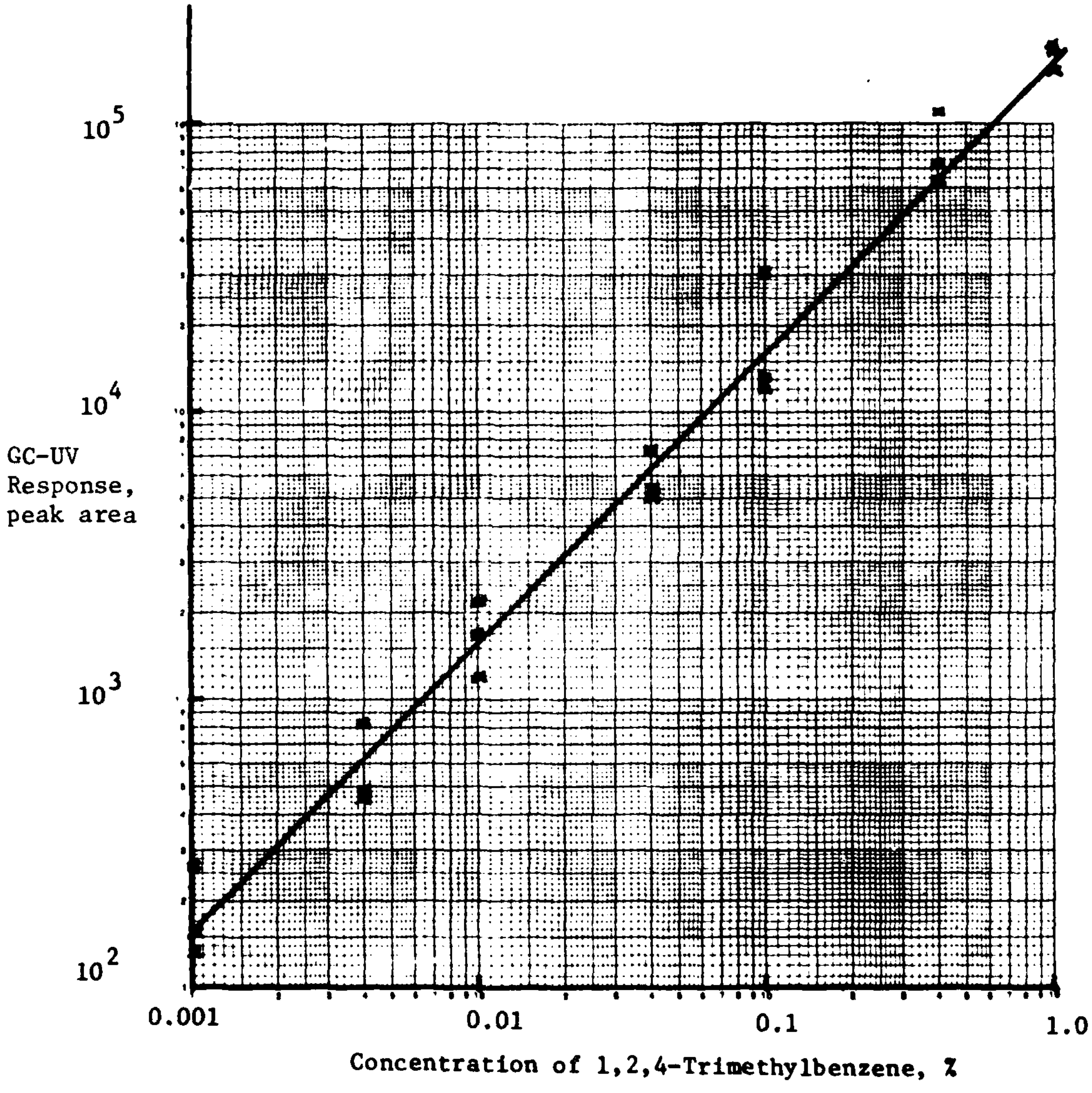


FIGURE 24. GC-UV RESPONSE OF 1,2,4-TRIMETHYLBENZENE

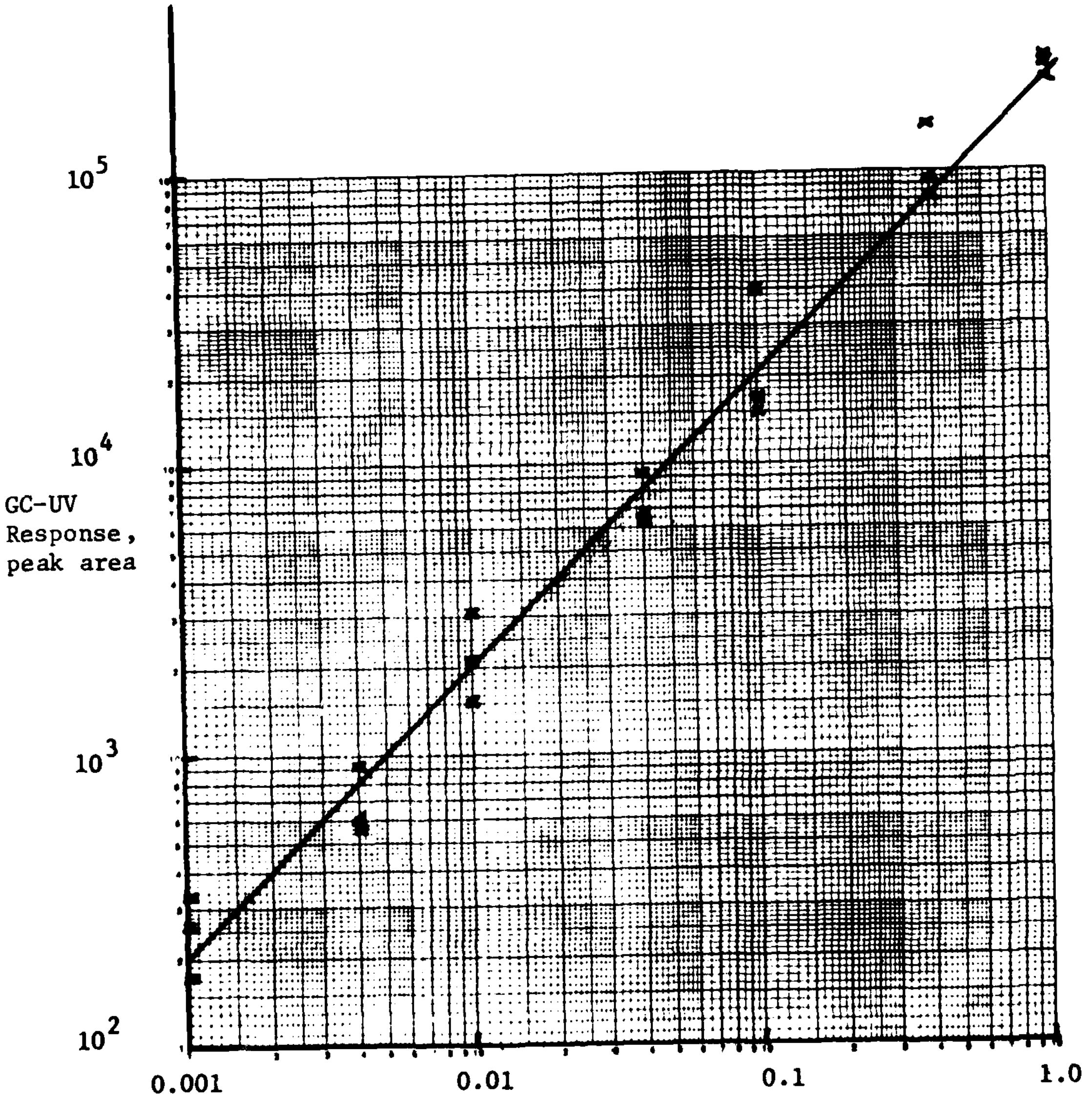


FIGURE 25. GC-UV RESPONSE OF 1,2,4,5-TETRAMETHYLBENZENE

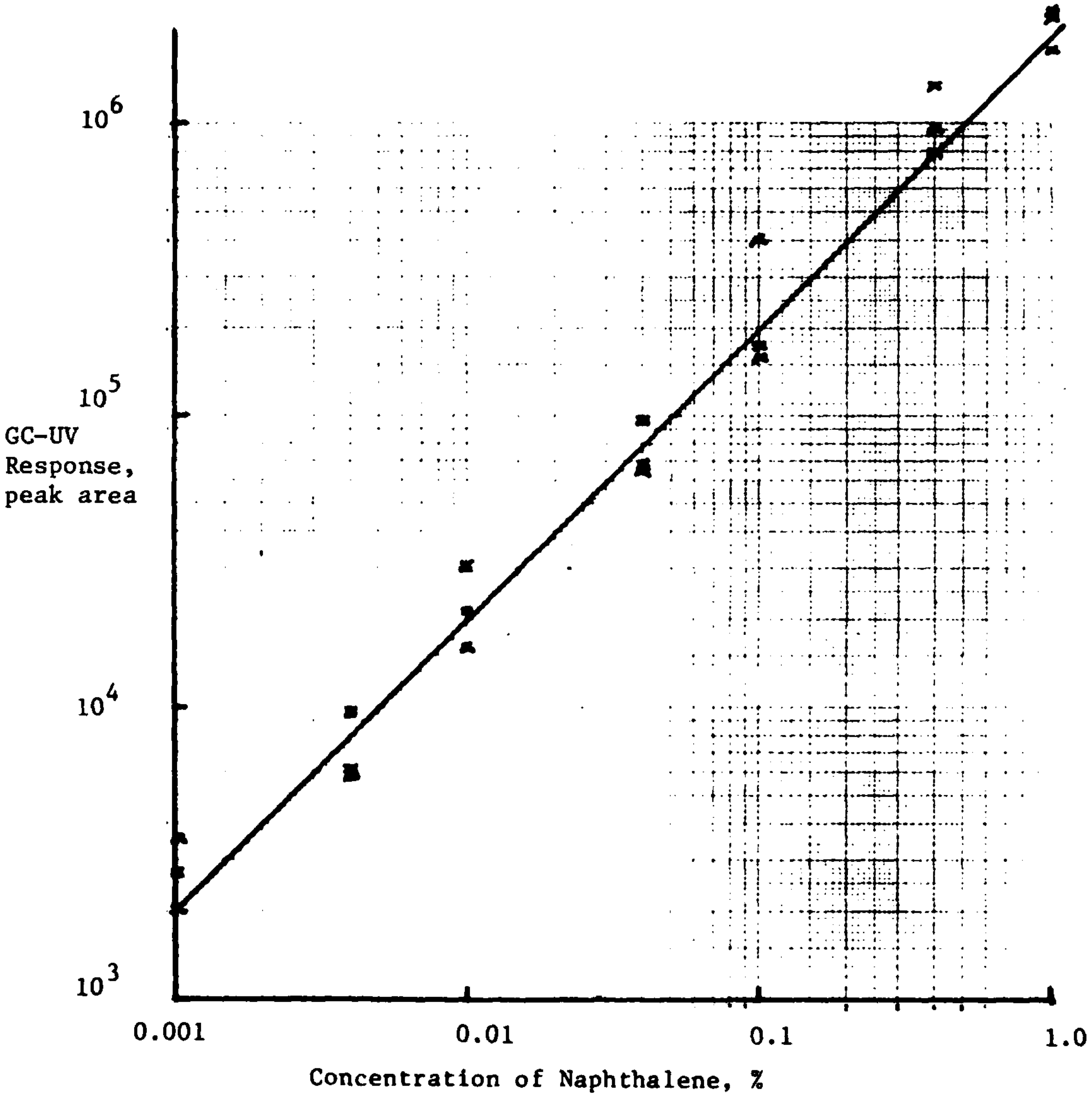


FIGURE 26. GC-UV RESPONSE OF NAPHTHALENE

TABLE 5. RELATIVE GC-UVD RESPONSE FACTORS FOR AROMATIC HYDROCARBONS

Concentration, %	GC Response Factor For Given Hydrocarbon[a]			
	Toluene	o-Xylene	Durene	Naphthalene
1.0	0.80 ± .12	0.97 ± 0.4	1.31 ± .02	12.2 ± .5
0.4	0.83 ± .04	0.97 ± .01	1.29 ± .02	12.5 ± .4
0.1	0.96 ± .10	1.02 ± .05	1.28 ± .03	12.9 ± .1
0.04	0.92 ± .08	1.02 ± .04	1.27 ± .01	12.9 ± .2
0.01	0.91 ± .04	1.01 ± .01	1.28 ± .06	13.0 ± .3
0.004	0.88 ± .11	1.09 ± .23	1.18 ± .05	12.5 ± .2
0.001	1.44 ± .50	1.09 ± .22	1.42 ± .12	15.7 ±1.5

a. Response relative to that of 1,2,4-trimethylbenzene determined at 208 nm; average of three determinations.

The precision of the detector was found to vary depending upon the width and height of the peak. The precision obtained for toluene which was an early-eluting and narrow peak was not as good as that obtained with the later-eluting compounds. Also, as expected, the precision of the very small peaks, i.e., those at the lowest concentration levels, was not as good as that for the more intense peaks. Considerably better precision may be obtainable in these cases by fine-tuning the Spectra-Physics Model 4000 data system that was used for this work. In most cases, however, i.e., other than for toluene and the low concentrations, the precision was <5%.

UV DETECTOR DESIGN

The Perkin Elmer GC-55 UV detector uses a deuterium arc light source, a grating monochromator, a 2.4 mm I.D. x 10 mm (45 μl) stainless steel cell with quartz windows, and a photodetector. The approach proposed for increasing the sensitivity of the system involves increasing the path length of the cell since absorbance and therefore sensitivity should be directly proportional to the path length. However, in order to avoid loss of GC resolution, it is necessary to keep the volume of the cell as low as possible. For example, to maintain the resolution achieved by a good capillary column, in which peak widths of one second are obtained, the cell volume of the detector should be such that the effluent from the column passes completely through the cell in one second. Based on a maximum flow rate of 2 ml/min (33 μl/sec) the cell volume should be no greater than 33 μl. This means that with a cell length of 10 mm an internal diameter of up to 2.05 mm can be used but as the length is increased to 50 mm or 100 mm the internal diameter must be kept below 0.92 mm and 0.65 mm, respectively. If the flow rate were reduced to 1 ml/min (16.7 μl/sec), the internal diameter for a 50-mm or 100-mm cell should be kept below 0.66 mm and 0.46 mm, respectively.

The use of relatively long cells with such small internal diameters creates major problems in terms of focusing enough light through the cell without getting excessive amounts of stray light that would give noise and without getting excessive losses to the walls. One approach is to use highly collimated light from a high-intensity xenon arc source. As long as the light does not strike the walls the cell could be made of metal, e.g. platinum-iriduim or passivated nickel, with quartz windows. The light could be directed to and from the cell by quartz fiber optics. A second approach is to focus the light from the existing deuterium source into the cell, which would give a relatively high input angle that would result in most of the light striking the walls of the cell. Losses to the walls would be minimized by constructing the cell of quartz and silvering it on the outside to reflect the light back into the cell. A third approach is a compromise in which the light from the existing deuterium source would be partially collimated and directed into a cell having an internal diameter as large as possible, e.g., 1.0 mm I.D. x 50 mm.

Some of the details involved in considering the second approach were given further study. Very severe constraints, 0.25 mm I.D.x 100 mm cell dimensions, were compared with less severe constraints, 0.75 mm I.D. x 100 mm cell dimensions. The cell dimensions control the light acceptance angle and hence the f number of the system. A 0.25 mm I.D. x 100 mm cell has a bore acceptance angle (see Figure 27) of $\theta = \frac{d}{L} = \frac{1}{400}$ rad, corresponding optically to an f/200 system. This means that the output of the monochromator would have to be collimated to f/200 with an image small compared to d. For an image size I, the useful angle is reduced further to (d-I)/L. In fact, the output of the monochromator supplied with the instrument to be used has an image roughly 10 mm x 0.5 mm and is collimated to about f/10. Direct coupling of this beam into the capillary can accomplish, at best, a throughput of only about 1%, determined solely by the ratio of bore area to image area. Nearly all of the light would be lost by wall absorption. No lens system can improve this because the f-number and area of the image are both larger than those of the capillary. A 0.75 mm I.D. cell, with a bore larger than the image width, could achieve nearly 10% throughput.

The throughput of the capillary cell could be increased if the acceptance angle of the cell could be increased to an effective f-number less than 10. Then, a relay lens could be used to reduce the image size while increasing the f-number back to 10, with a corresponding increase in throughput. The acceptance angle of the capillary can be effectively increased by use of a reflective coating on the outside of the capillary, where it will not come into contact with the gases being tested. In order to evaluate this possibility, a simple model was set up. The geometry used is shown in Figure 28. For simplicity, only the meridional rays were treated, i.e., rays which intersect the capillary axis. Let the index of refraction in the wall be n, the wall thickness be t, the wall loss (per cm) be α, and the reflection coefficient at the outer coating be r. We ignore the Fresnel reflections at the bore-wall interface; this will give us a pessimistic estimate.

Applying Snell's law at the bore-wall interface gives for the horizontal path length for one reflection

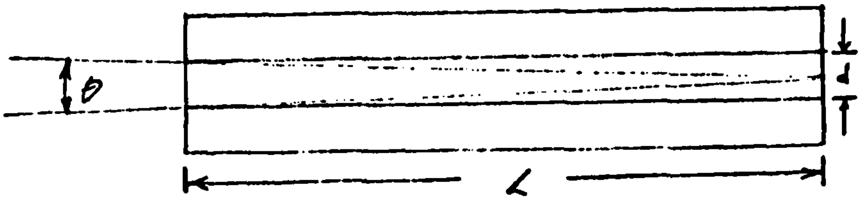


FIGURE 27. SCHEMATIC OF A CELL UTILIZING AN UNCOATED CAPILLARY. (Illustrating the low acceptance angle of such cell designs).

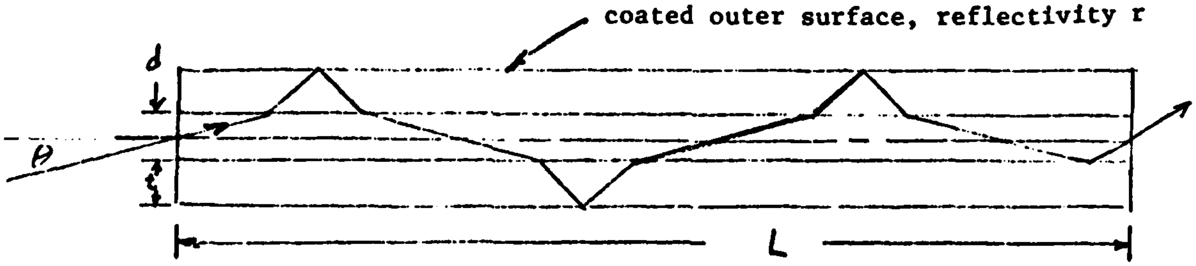


FIGURE 28. SCHEMATIC OF A CELL UTILIZING A COATED CAPILLARY. (Illustrating the path of a typical (meridional) ray through the cell and the increased acceptance angle).

$$\ell = D\cot\theta + 2t\,\tan(\sin^{-1}\frac{1}{n}\cos\theta).$$

The number of reflections is, then,

$$N(\theta) = \frac{L}{\ell} = \frac{A\tan\theta}{(1 + 2\rho\, B(\theta))}$$

where

$$A = \frac{L}{d}\ , \quad \rho = {}^{t}/D$$

and

$$B(\theta) = {}^{\sin\theta}/\sqrt{n^2 - \cos^2\theta}$$

The actual path length in the wall is

$$p_w = 2t\,\sec(\sin^{-1}\frac{1}{n}\cos\theta)$$

$$= 2nt/\sqrt{n^2 - \cos^2\theta}$$

The light intensity transmitted through one reflection is, then, determined by

$$r_{eff} = r\, e^{-\alpha p_w}$$

and the overall transmission is

$$T(\theta) = (r_{eff})^{N(\theta)}$$

Of the horizontal path length, only that part during which the light is in the capillary bore is effective. This fraction is

$$f_b = [1 + 2\, n\, \rho\, B(\theta)]^{-1}$$

We can now construct a figure of merit for the coated cell by taking the average of $f_b T$ over input angles:

$$F = \langle f_b T \rangle = \int_o^{\theta_{max}} (r_{eff})^{N(\theta)} [1 + 2\, n \rho\, B(\theta)]^{-1} \sin\theta d\theta / (1-\cos\theta_{max})$$

where we have taken the power in as emanating from a point source of radiant intensity J, so that

$$dP_{in} = 2\,\pi\, J \sin\theta d\theta$$

The average is then defined by

$$\langle \ldots \rangle = \int_o^{\theta_{max}} (\ldots) dP_{in} / \int_o^{\theta_{max}} dP_{in}$$

The formulae derived above were evaluated numercially for a 100-mm path length and capillary inner bores of 0.25, 0.50, and 0.75 mm, giving A = 400, 200, and 133, all for $\rho = 1.0$ (the commercial standard) and $n = 1.5$. For each A, values of r_{eff} of 0.98, 0.95, and 0.90 were used. For a non-adsorbing wall material, $r_{eff} = .98$ would correspond to a good silver coating, while $r_{eff} = 0.90$ would correspond to a good aluminum coating. In Figure 29 are shown the transmission through the capillary versus input angles, Θ. In Figure 30 are shown the curves for the $f_b T$ versus the maximum input angle. The two sets of curves are very similar, and point up the strong dependence of performance improvement on r_{eff}. If we are to have $r_{eff} = .95$ or .90, we would have to have absorption coefficients α as shown in Table 6, (we ignore the angular dependence of r_{eff} and use the value for $\Theta = 0$).

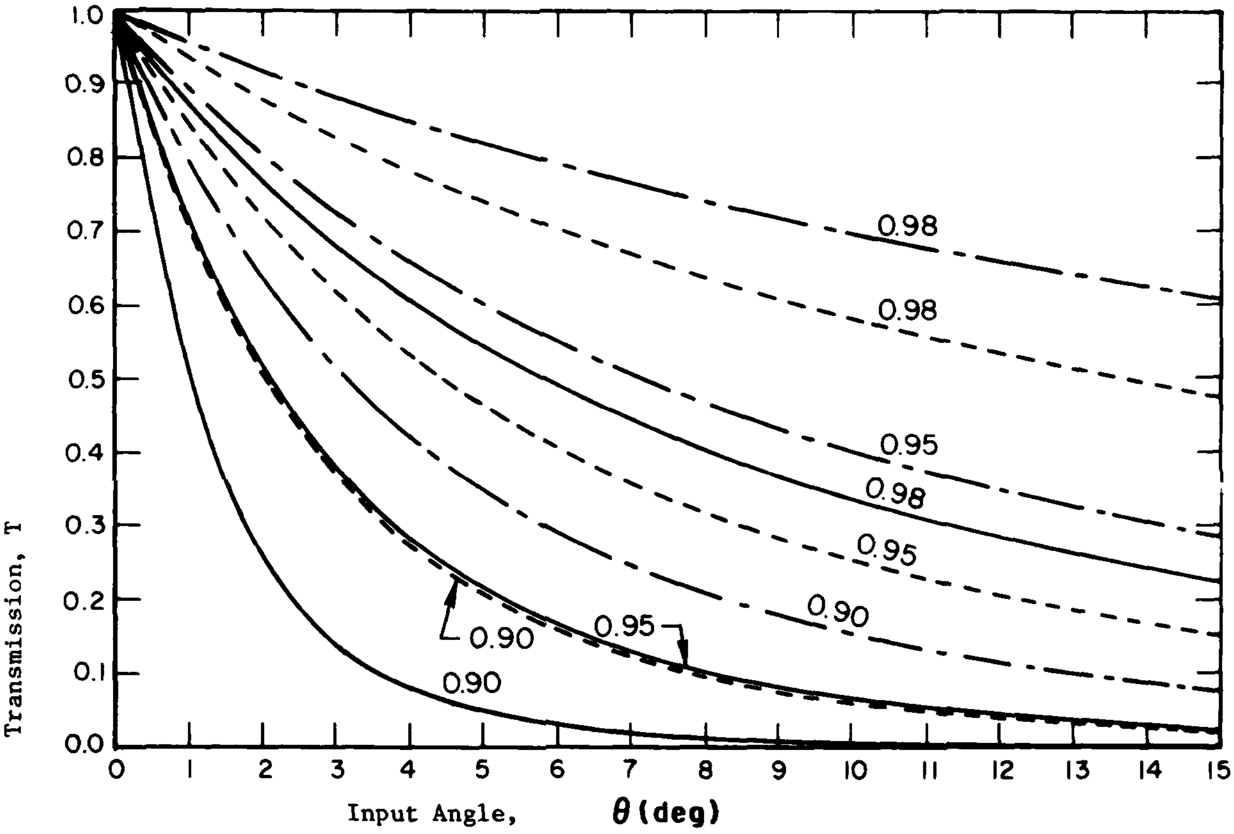


FIGURE 29. TRANSMISSION OF MERIDIONAL RAYS THROUGH A COATED CAPILLARY VERSUS INPUT ANGLE. (The figures on the curves are the effective reflectivities at the quartz-metal interface. (———) L/d = 400; (--------) L/d = 200; (—— -——) L/d = 133.

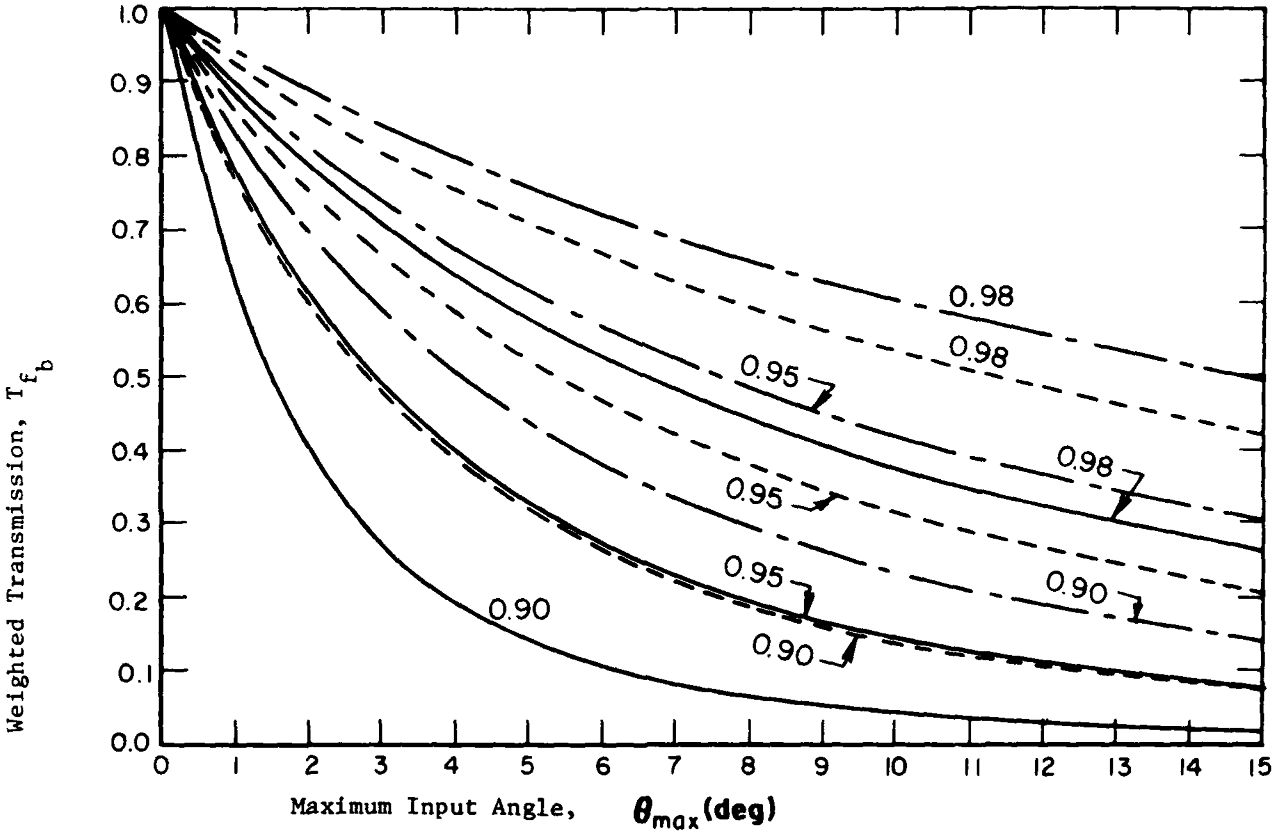


FIGURE 30. WEIGHTED TRANSMISSION OF MERIDIONAL RAYS THROUGH A COATED CAPILLARY VERSUS MAXIMUM INPUT ANGLE. (The figures on the curves are the effective reflectivities at the quartz-metal interface. (———) L/d = 400; (-------) L/d = 200; (—— - ——) L/d = 133. The transmission is weighted by the fraction of light path that lies in the capillary bore, f_b, and averaged over input angles.

TABLE 6. REQUIRED ABSORPTION COEFFICIENTS

r_{eff}	Required Absorption Coefficients, α (cm^{-1}), For Cell With Given I.D.		
	0.25 mm	0.50 mm	0.75 mm
.95	0.41	0.20	0.14
.90	1.10	0.56	0.37

At a light wavelength of 200 nm, optical grade fused quartz has a transmission of 13% through a 1 cm sample, corresponding to $\alpha = 2.0$ cm^{-1}. Hence, we will need to use capillaries of special u.v. materials, such as Suprasil 1, which has a transmission of 91% at 200 nm, corresponding to $\alpha = 0.095$ cm^{-1}. This value is low enough that the reflection coefficient of the coating will be the limiting parameter.

It should be noted that the path length of the light in the bore is larger than the horizontal path length in the bore ($=N(\Theta)D\cot\Theta$) used in calculating f_b. Since the overall sensitivity of the GC system is fixed by the bore path length, it is of some interest to evaluate it. We have, for one reflection,

$$p_b = D\csc\Theta$$

so, for N(Θ) reflections,

$$P_b = N\ (\Theta) D\csc = \frac{L\sec\Theta}{1+2\rho B(\Theta)}$$

It is easily shown that the average $T\ P_b/L$, taken as in the above equation, is larger than $T\ f_b$ considered above. Hence, optimizing $T\ f_b$ will automatically tend to increase the sensitivity of the system, for a fixed L. Over the range of angles of interest here, the difference between the two averages is small, and we can consider them as optimized simultaneously. Hence, on this model, the sensitivity, as measured by path length, need not be considered separately.

Some measurements of a preliminary nature were carried out on capillaries of 0.25 mm and 0.75 mm bore diameters and varying length, in the wavelength range from 350 nm to 800 nm. The setup is pictured schematically in Figure 31. Light from an Xe light source passes through a grating monochromator, a lens, and an iris. The iris determines the f/number of the incident radiation. The light is focused in the plane of a pinhole whose diameter is equal to that of the capillary bore, and the capillary is placed in behind the pinhole and aligned with it. The purpose of the pinhole is to guard against having light incident on the capillary end, since such light will be carried down the capillary wall without entering the bore; such light would cause erroneously high measured transmission. The transmission is measured as the ratio of light at the detector with and without the capillary present.

The results of these first measurements indicated that the alignment of the capillary with the pinhole was probably poor, especially for the 0.25 mm bore. Coating the capillary input end with silver or some other opaque material will be used to prevent the spurious light from entering the wall. At the same time, the wavelength range will be moved towards the 200 nm region. It is likely, on the basis of these calculations and experiments and consideration of the mechanical problems associated with gas transport to and from the cell, that a 0.50 to 0.75 mm I.D. capillary will be selected for the final cell design instead of a smaller-bore capillary. We have obtained such capillaries made from Supracil, a special u.v. grade silica, for this work.

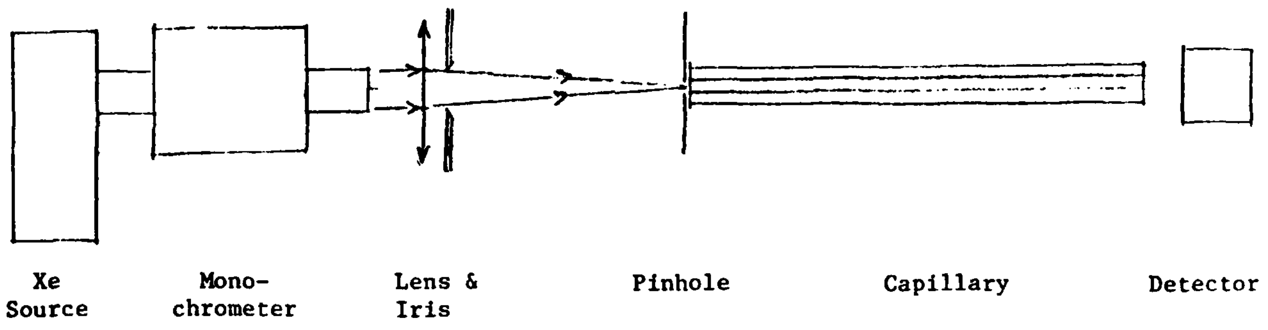


FIGURE 31. EXPERIMENTAL SETUP FOR INITIAL TRANSMISSION EXPERIMENTS

Photoionization Detector Studies

A photoionization detector (PID) was evaluated to determine whether it could be used as a selective detector for aromatic hydrocarbons in fuels. The particular detector used was an HNV Systems Model PI-52 equipped with a 9.5 e.v. source. Since the saturated hydrocarbons have ionization potentials of about 10 e.v. and the aromatic hydrocarbons have ionization potentials of about 8.5 e.v., the 9.5 e.v. source should ionize the aromatic hydrocarbons preferentially and thus provide a selective response.

The response of the PID was evaluated using four saturated hydrocarbons, namely n-heptane, n-octane, n-dodecane, and bicyclohexyl and six aromatic hydrocarbons, namely toluene, o-xylene, pseudocumene(1,2,4-trimethylbenzene), durene(1,2,4,5-tetramethylbenzene), naphthalene, and 2-methylnaphthalene. The detector was interfaced with a Varian Model 1740 gas chromatograph fitted with a 30 m SE-30 W.C.O.T glass capillary column. The compounds were dissolved in petroleum ether in concentrations ranging from 0.001% to 0.4% and 2 μl was injected into the system with a split ratio of 10:1.

The response versus concentration was not a linear function for any of the compounds as indicated by the fact that the log-log plots, given in Figures 32 to 41, have slopes that deviate a considerable amount from unity. In general the slopes of the response curves were almost unity at the two or three highest concentrations but increased for the lower concentrations. Heptane and octane behaved differently in that the slopes of the response curves were less than unity at the high concentrations but increased dramatically at low concentrations. The PID is claimed by the manufacturer to have a linear response range of 10^5. The nonlinearity observed in our study may be partly due to nonlinearity in the splitter or to nonlinearity of dilution.

Response factors, determined as response relative to that of pseudocumene, were calculated for the various compounds studied and are given in Tables 7 and 8. Although the precision of any given response factor, based on triplicate detrminations, was generally <10%, the response factors for any given hydrocarbon varied considerably over the concentration range of 0.001 to 0.4%.

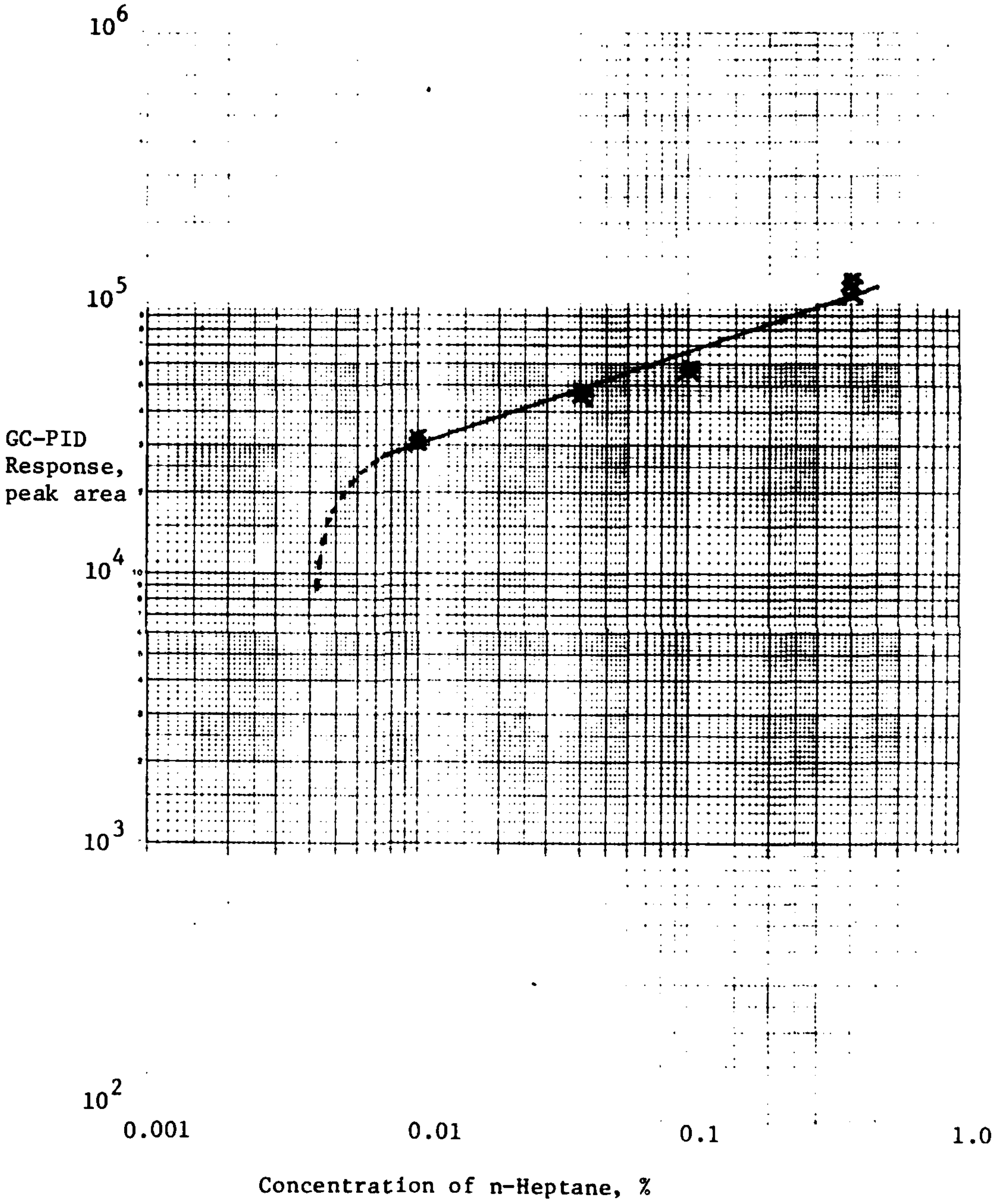


FIGURE 32. GC-PID RESPONSE OF n-HEPTANE

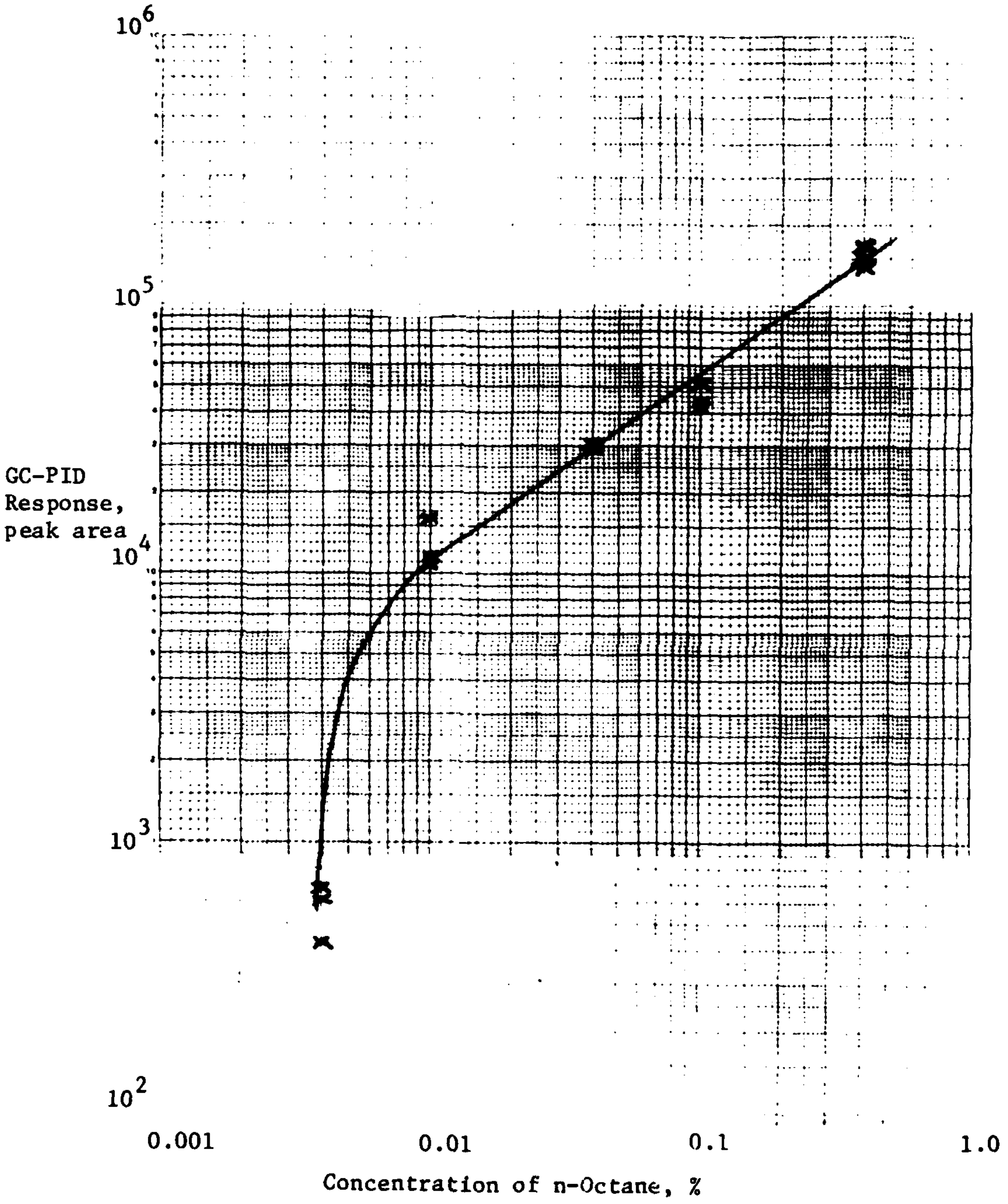


FIGURE 32. GC-PID RESPONSE OF n-OCTANE

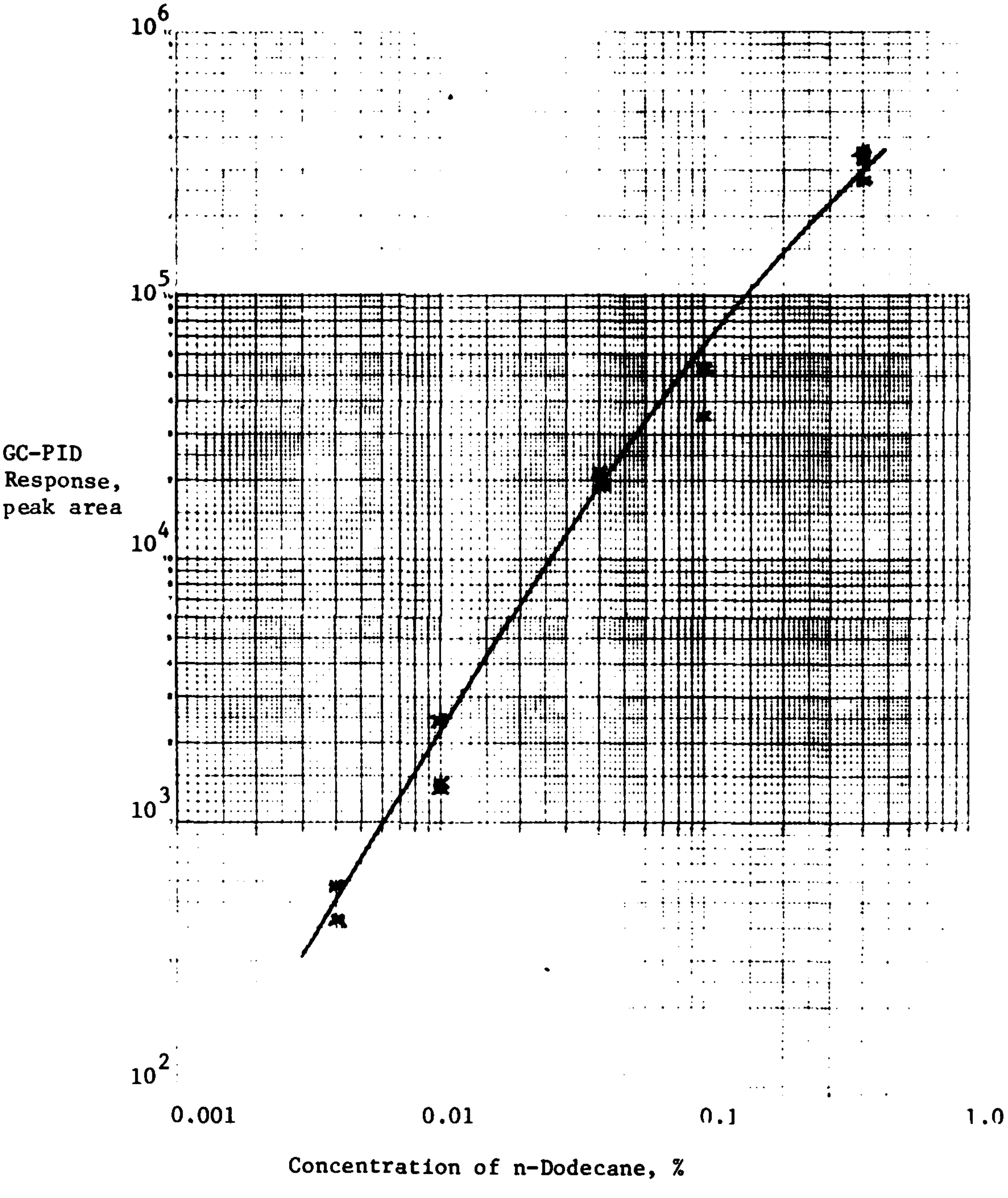


FIGURE 34. GC-PID RESPONSE OF n-DCDECANE

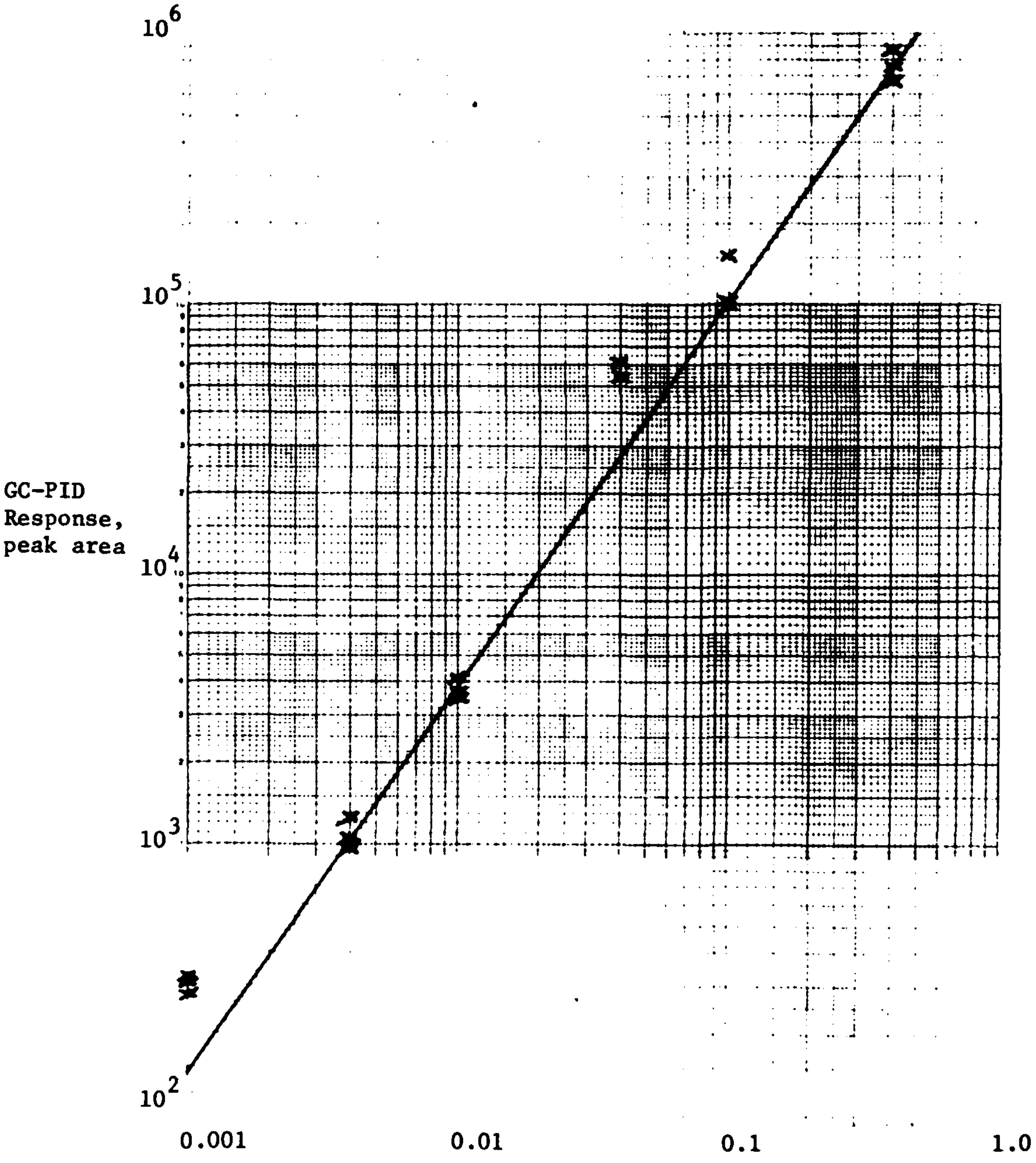


FIGURE 35. GC-PID RESPONSE OF BICYCLOHEXYL

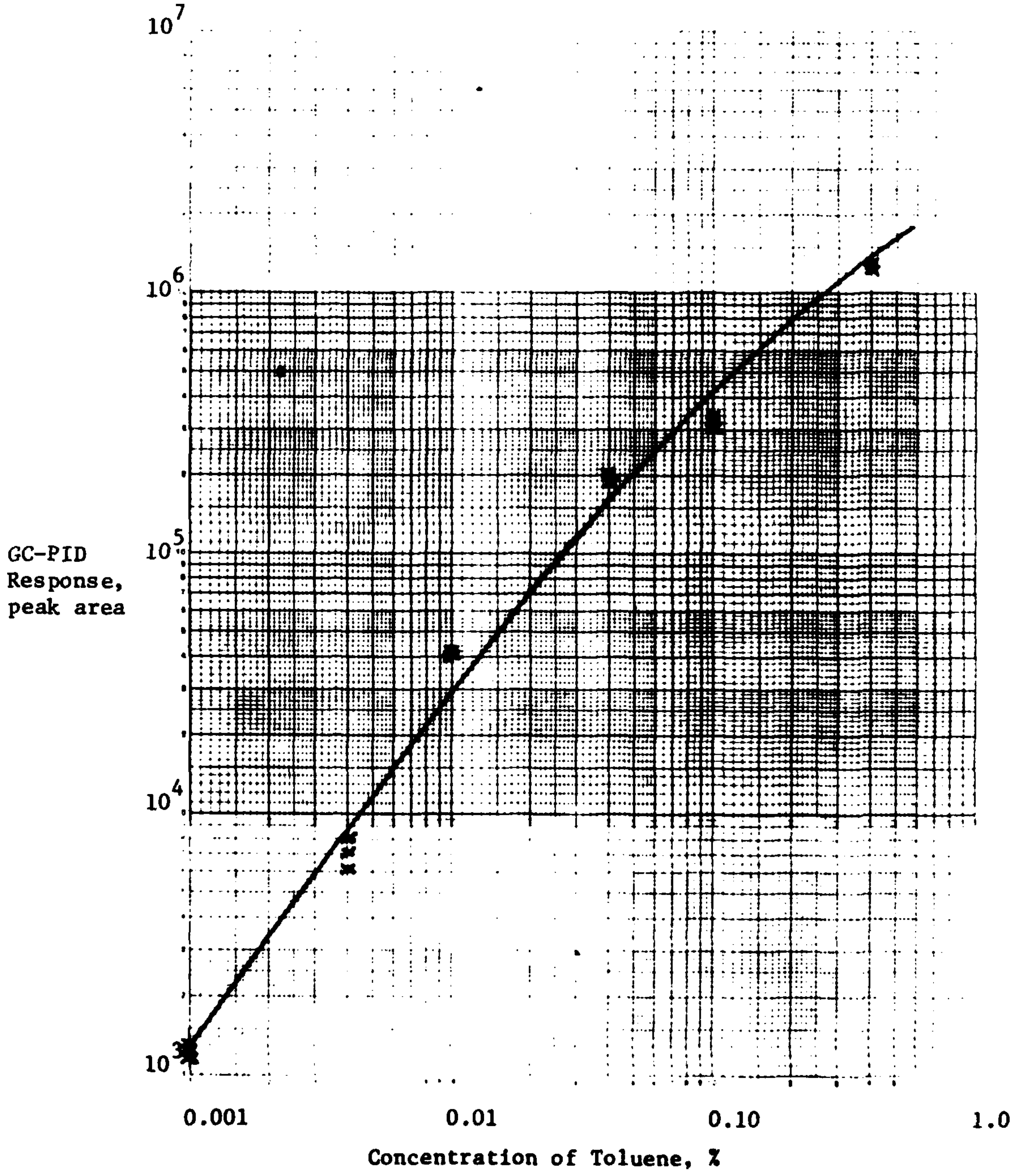


FIGURE 36. GC-PID RESPONSE OF TOLUENE

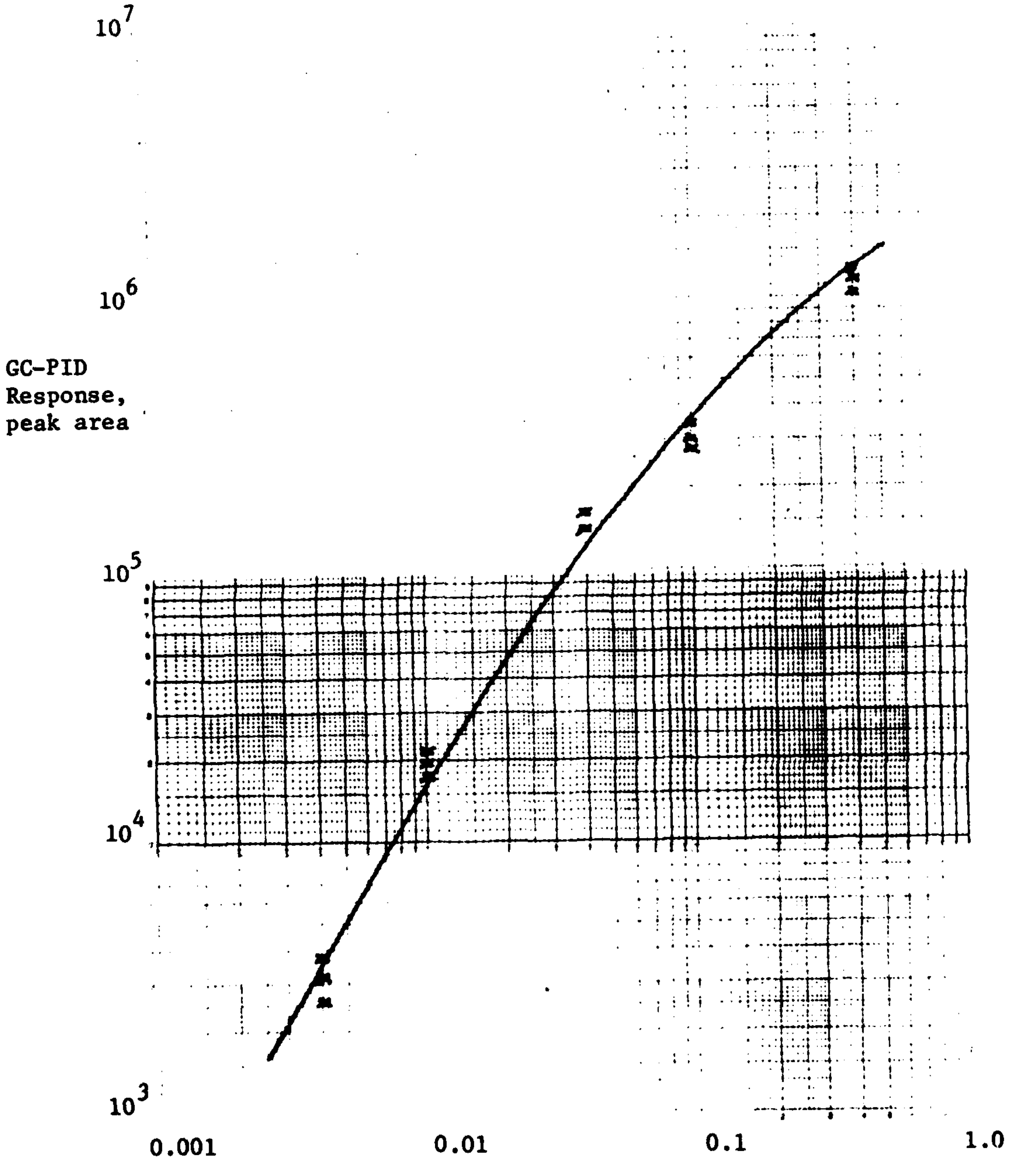


FIGURE 37. GC-PID RESPONSE OF o-XYLENE

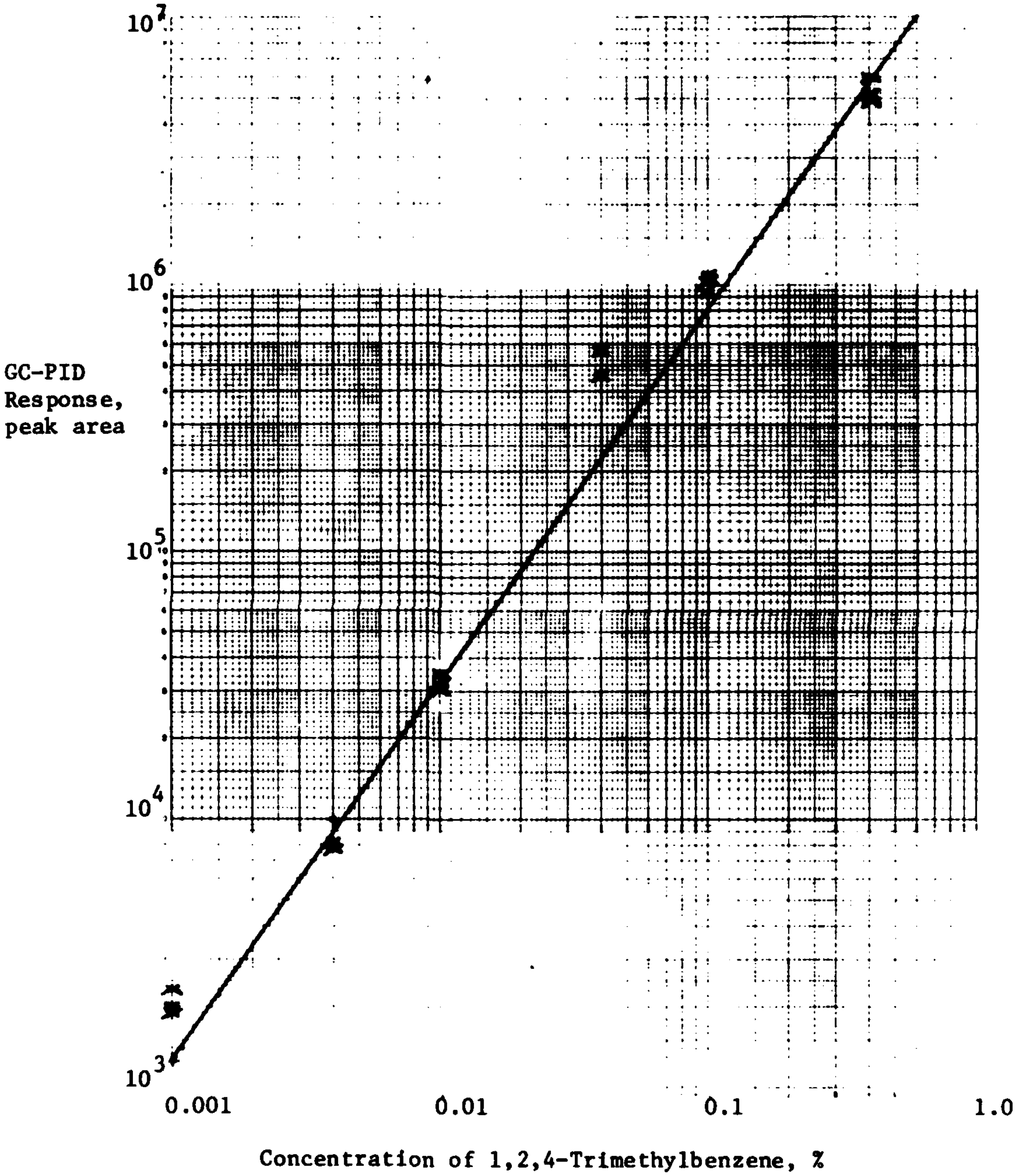


FIGURE 38. GC-PID RESPONSE OF 1,2,4-TRIMETHYLBENZENE

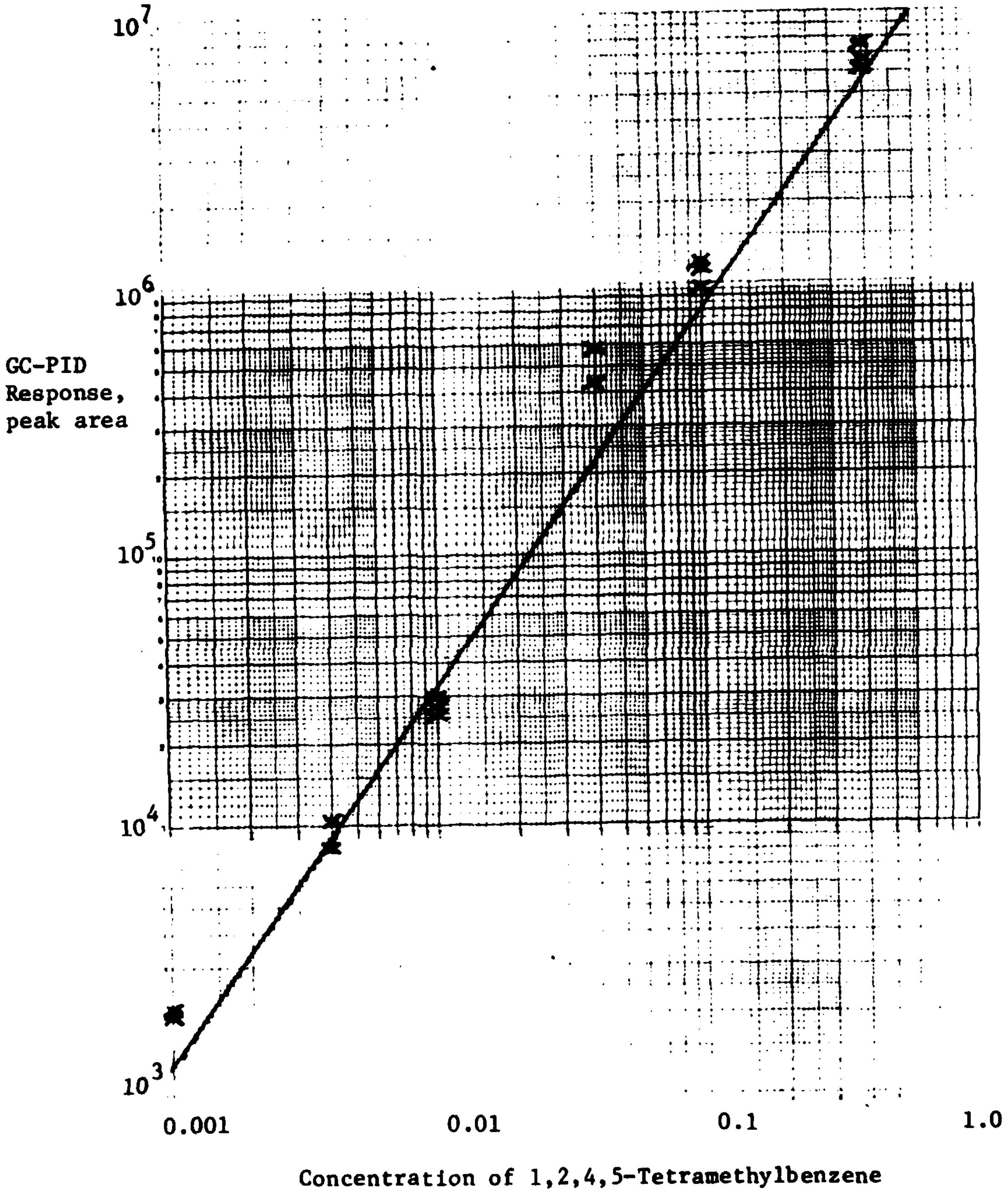


FIGURE 39. GC-PID RESPONSE OF 1,2,4,5-TETRAMETHYLBENZENE

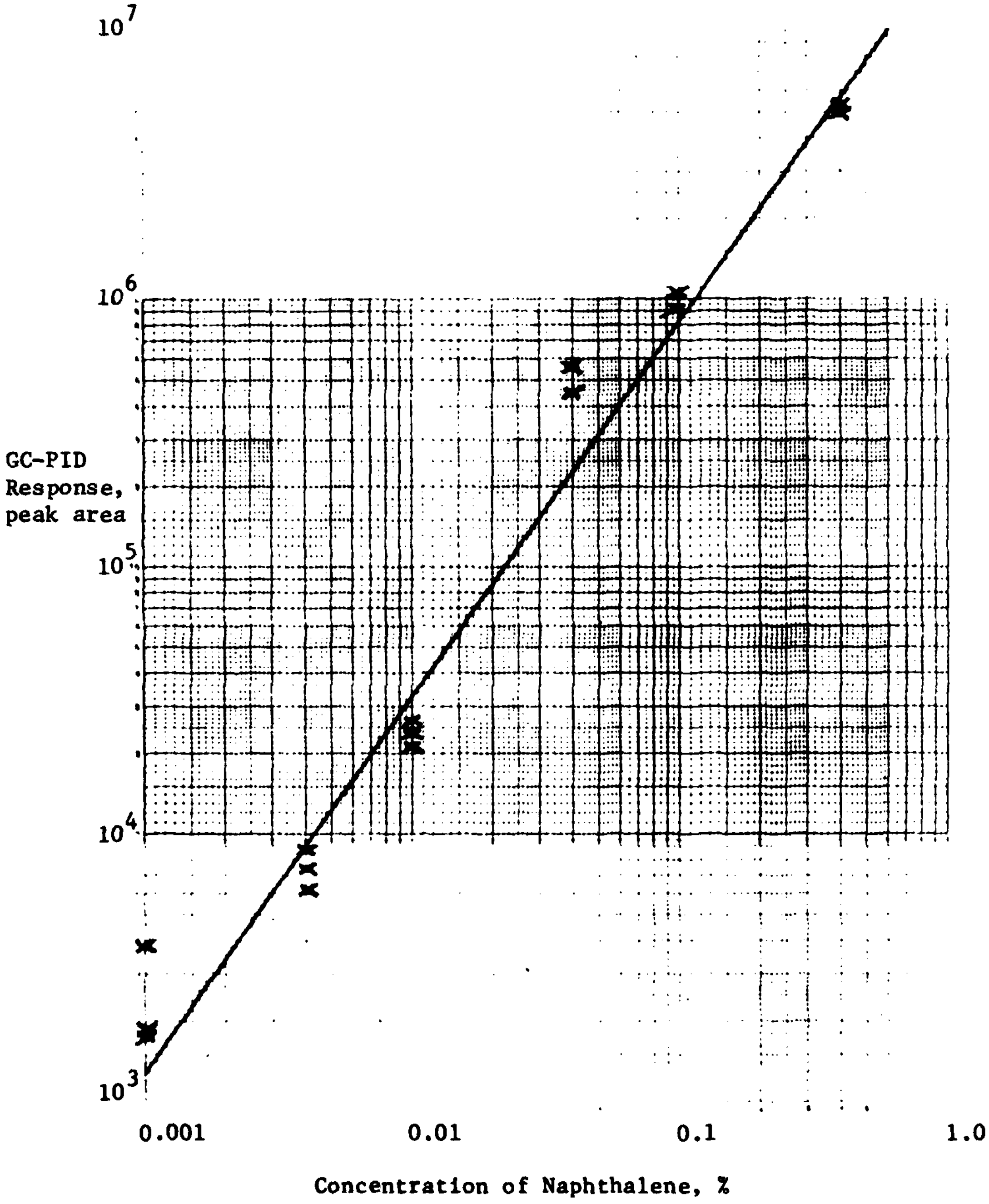


FIGURE 40. GC-PID RESPONSE OF NAPHTHALENE

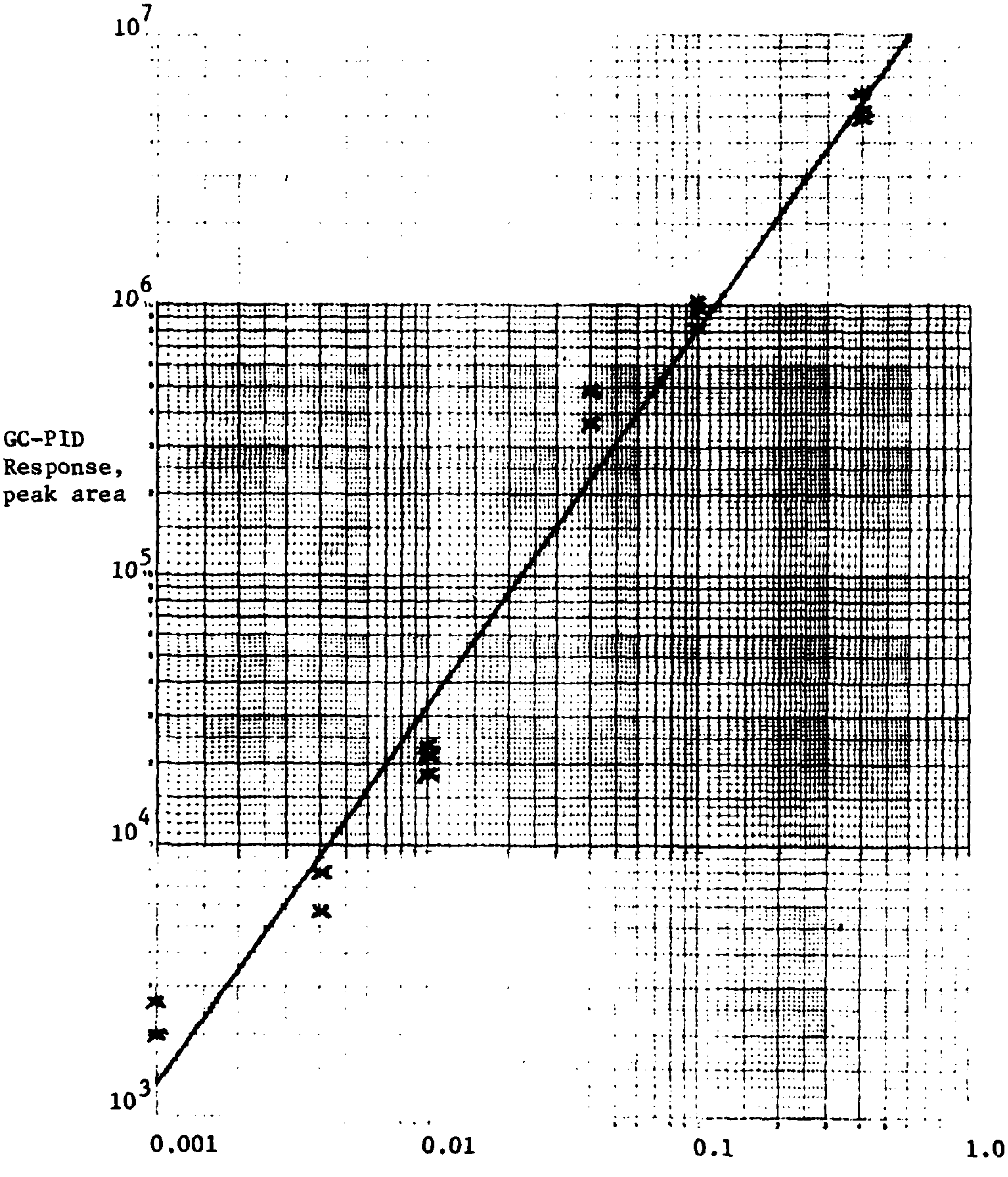


FIGURE 41. GC-PID RESPONSE OF 2-METHYLNAPHTHALENE

TABLE 7. RELATIVE GC-PID RESPONSE FACTORS FOR SATURATED HYDROCARBONS

	GC-PID Response Factor for Given Compound[a]			
Concentration, %	Heptane	Octane	Dodecane	Bicyclohexyl
0.4	0.02	0.03	0.06	0.15
0.1	0.06	0.04	0.04	0.11
0.04	0.09	0.06	0.04	0.11
0.01	0.97	0.46	0.05	0.12
0.004	--	0.07	0.06	0.13
0.001	--	--	--	0.15

a. Response relative to that of 1,2,4-trimethylbenzene; average of three determinations.

TABLE 8. RELATIVE GC-PID RESPONSE FACTORS FOR AROMATIC HYDROCARBONS

	GC-PID Response Factor for Given Compound[a]				
Concentration, %	Toluene	o-Xylene	Durene	Naphthalene	2-Methyl-naphthalene
0.4	0.24	0.22	1.33	1.03	1.03
0.1	0.32	0.26	1.09	0.98	0.89
0.04	0.38	0.29	0.97	0.98	0.83
0.01	1.29	0.56	0.88	0.75	0.65
0.004	0.84	0.36	1.07	0.87	0.77
0.001	0.59	0.29	1.09	0.93	0.85

a. Response factor relative to that of 1,2,4-trimethylbenzene; average of three determinations.

The degree of selectivity achieved can be determined from the response factors. The detector was most sensitive for durene, naphthalene, 2-methylnaphthalene, and psuedocumene. These four compounds had similar responses which were approximately 4 times the responses of toluene and o-xylene, 8 times the response of bicyclohexyl, and 25 times the responses of n-heptane, n-octane, and n-dodecane. The relative responses thus provided some degree of selectivity in favor of aromatic hydrocarbons versus saturated hydrocarbons but not enough to permit only aromatic hydrocarbons to be seen in a PID chromatogram of a jet fuel. The PID chromatograms obtained for two representative jet fuels, syncrude JP-4 and Paraho JP-4, are shown in Figures 42 and 43, respectively. The chromatogram of Paraho JP-4 clearly shows the relatively large amounts of naphthalenes; however, the chromatogram of syncrude JP-4, relatively low in naphthalenes, gives no indication of such an aromatic pattern. The inadequate selectivity of the PID make it of very little use for the characterization of aromatic components in whole jet fuels.

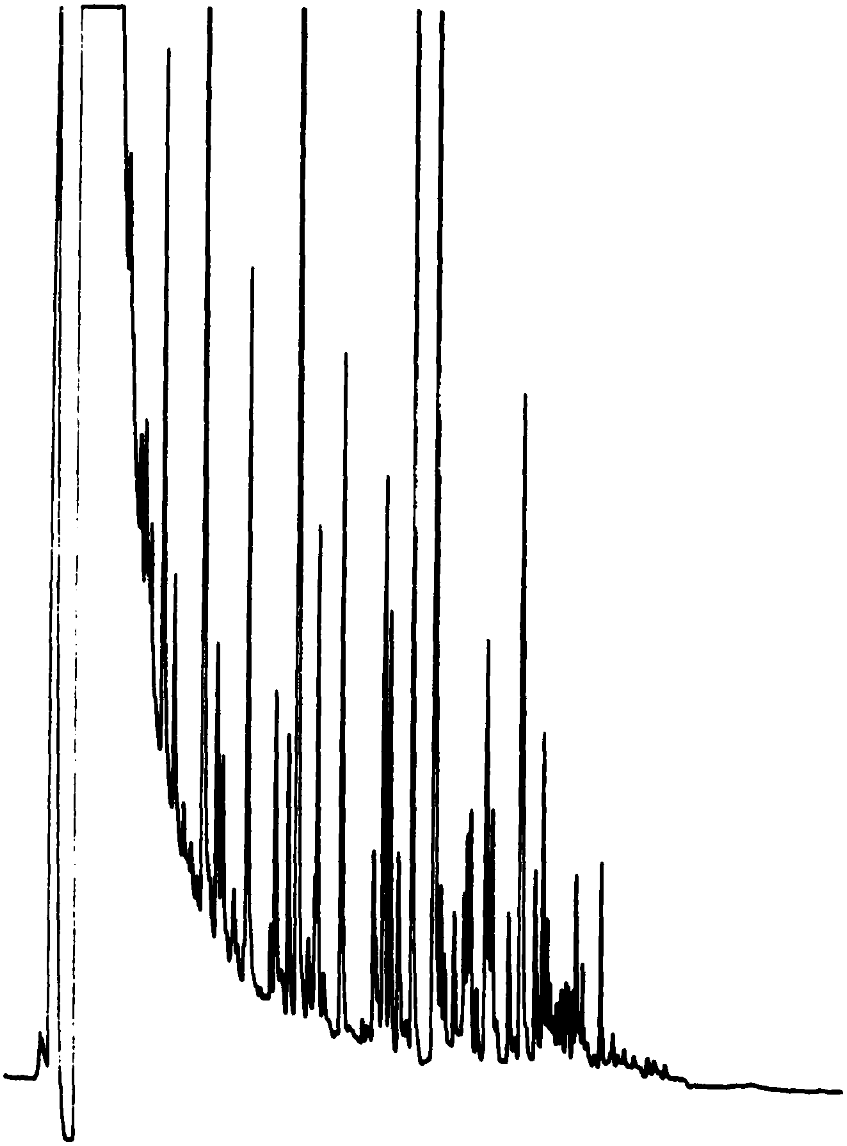
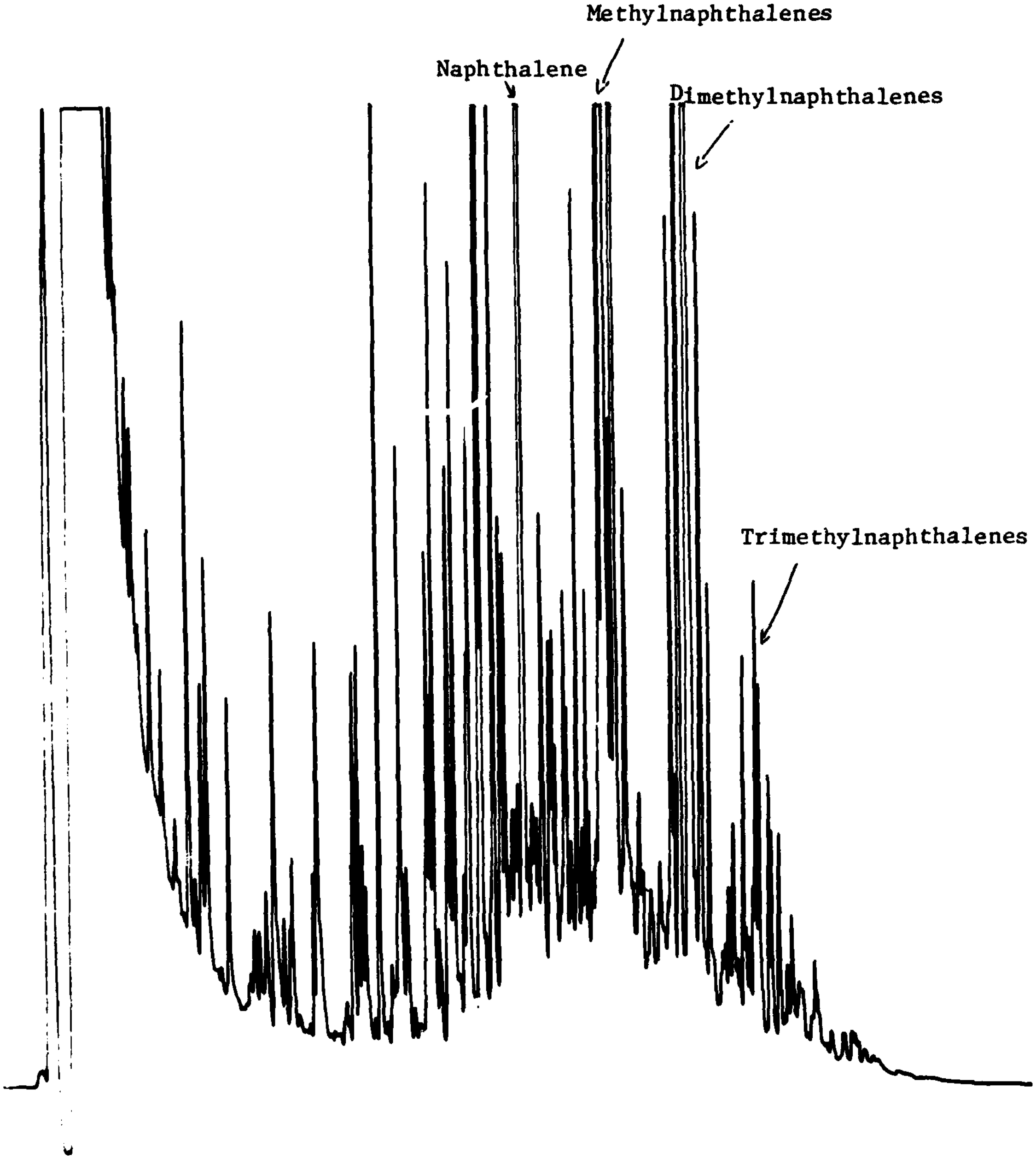


FIGURE 42. CAPILLARY COLUMN GAS CHROMATOGRAM OF SYNCRUDE JP-4 USING PHOTOIONIZATION DETECTOR



[illegible] . CAPILLARY COLUMN GAS CHROMATOGRAM OF PARAHO JP-4 USING PHOTOIONIZATION DETECTOR

CONCLUSIONS AND RECOMMENDATIONS

The results obtained on this program indicate that a modified Perkin Elmer Model GC-55 ultraviolet detector used with a glass capillary column gas chromatograph will probably serve exceptionally well as a rapid and effective method for determining most of the aromatic components in aircraft fuels. Similar results can be achieved by fractionating the fuels using silica gel and analyzing the resulting aromatic fraction by glass capillary column gas chromatography using a flame ionization detector. The latter method, however, is considerably more involved and time-consuming than the GC-UVD approach. The photoionization detector does not appear to be suitable as a specific detector for aromatic components in fuels.

Recommendations for further studies include:

1. Replace the stainless steel transfer line in the UVD with a glass capillary transfer line.
2. Design and evaluate a 1.0 mm I.D. x 50 mm cell for the UVD.
3. Study silvered quartz capillaries as long-path-length and low-volume UVD cells.
4. Determine the precision, accuracy, and sensitivity of the UVD at various wavelengths for the determination of model compounds.
5. Quantitate the major aromatic components in a variety of aircraft fuels using the UVD.
6. Evaluate a nitrogen-specific thermionic detector for the GC analysis of aircraft fuels.
7. Evaluate a sulfur-specific flame photometric detector for the GC analysis of aircraft fuels.
8. Connect the UVD in parallel or in series with a flame ionization detector and evaluate the system for analyzing aircraft fuels.

APPENDIX A

TENTATIVE METHOD FOR SEPARATION OF AROMATICS AND NONAROMATICS IN PETROLEUM PRODUCTS

(Battelle's Columbus Laboratories, 10-1-78)

Scope and Application

1. (a) This method covers the separation of aromatics from nonaromatics in gasoline, fuel oils, and crude oils.

(b) Pentane-insoluble components are removed by centrifugation prior to the separation.

(c) The separated aromatic and nonaromatic fractions obtained can be used directly without concentration for GC analysis of all components that boil above 75° C.

Summary

2. The sample dissolved in n-pentane is introduced to a glass chromatographic column packed with activated silica gel. The nonaromatics are eluted first with n-pentane and the aromatics are eluted second with methylene chloride.

Definitions

3. (a) Nonaromatics are comprised of the paraffinic, naphthenic and olefinic hydrocarbons.

(b) Aromatics are comprised of aromatic hydrocarbons, condensed naphthenic aromatic hydrocarbons, aromatic olefins, and some of the less polar heterocyclic compounds such as benzothiophenes and carbazoles.

Apparatus and Reagents

4. (a) Chromatographic Column, 250 mm x 9 mm O.D. glass column fitted with a sintered glass disc and teflon stopcock at the bottom.

(b) Centrifuge, capable of handling standard 15-ml centrifuge tubes at 3000 RPM.

(c) Centrifuge tubes, 15-ml, glass, calibrated, conical type.

(d) Syringe, 250-μl.

(e) Syringe, 2 ml.

(f) Graduated Cylinder, 100-ml.

(g) Collection bottles, 30-ml, narrow-mouth, glass, with teflon-lined screw cap.

(h) Beaker, 100-ml.

(i) Silica gel, *100-200 mesh, Davison Grade 923, activated in an open* container in an oven at 150 C for at least 16 hours but no more than 80 hours.

(j) Methylene Chloride, Burdick and Jackson distilled-in-glass grade or equivalent.

(k) Pentane, Burdick and Jackson distilled-in-glass grade or equivalent.

Procedure

5. (a) Suspend 10 g of silica gel in 20 ml of methylene chloride in a 100-ml beaker.

(b) Pour the slurry into the chromatographic column with the stopcock open.

(c) Wash the remaining silica gel onto the column with another 20 ml of methylene chloride. Allow the liquid level to move down nearly to the top of the silica gel (within 1 mm) and close the stopcock.

(d) Rinse the top of the column with 2 ml of pentane and open the stopcock to again allow the liquid level to move down nearly to the top of the silica gel. Make sure the solvent level in the column never goes below the silica gel level during the entire silica gel procedure. Repeat this rinse step using 2 ml and again using 35 ml of pentane.

(e) Add 250 µl of sample if nonviscous or 250 mg of sample if too viscous for syringe sampling to 10 ml of pentane contained in a glass stoppered centrifuge tube. Mix thoroughly by repeated inversions. If insoluble material is present, centrifuge for 15 minutes at approximately 3000 RPM.

(f) Apply 2.0 ml of the pentane solution of the sample, using a syringe, to the top of the chromatographic column and allow the liquid level to move down nearly to the top of the silica gel.

(g) Fill the syringe with 2 ml of pentane, apply this to the column, and again allow the liquid level to move down nearly to the top of the silica gel. Repeat this step once more. Discard all eluates up to this point.

(h) Elute with 20 ml of pentane followed by 30 ml of methylene chloride.

(i) Collect two 25-ml eluate fractions. The first fraction contains the nonaromatics and the second fraction contains the aromatics.

☆U.S.Government Printing Office: 1980 — 657-084/740

ILMED

-8